



**Università di Trieste**  
**Corso di Laurea in Geologia**

**Anno accademico 2015 - 2016**

**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):



Other common hydrocarbon gases are:

**ethane** ( $\text{C}_2\text{H}_6$ ), **propane** ( $\text{C}_3\text{H}_8$ ) **butane** ( $\text{C}_4\text{H}_{10}$ )

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:



# 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

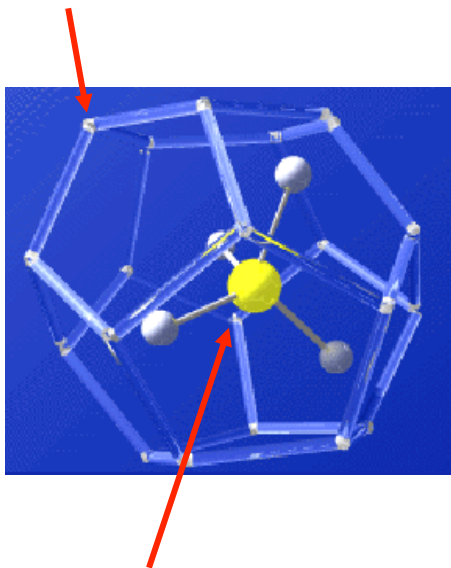
- **Wetlands**
- **Termites**
- **Oceans** (*anaerobic digestion in marine zooplankton and fish, and also from methanogenesis in sediment*)
- **Hydrates**
- **Juvenile**

# HYDRATES OF NATURAL GAS

*(discovered in 1810)*

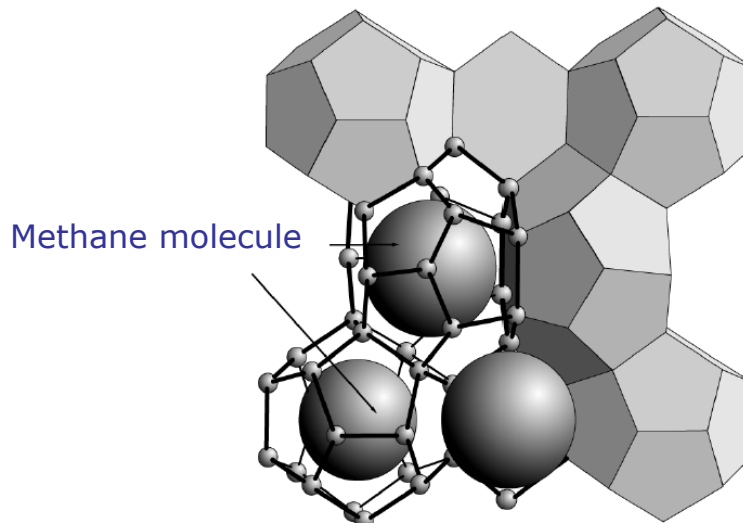
- Gas hydrates are a **solid phase** composed of **water** and low-molecular weight **gases** (predominantly methane)
- Water molecules form an ordered crystalline solid matrix which includes gas molecules with weak electro-static bounds
- The state of **saturation of hydrates is a function of pressure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

## Water molecule

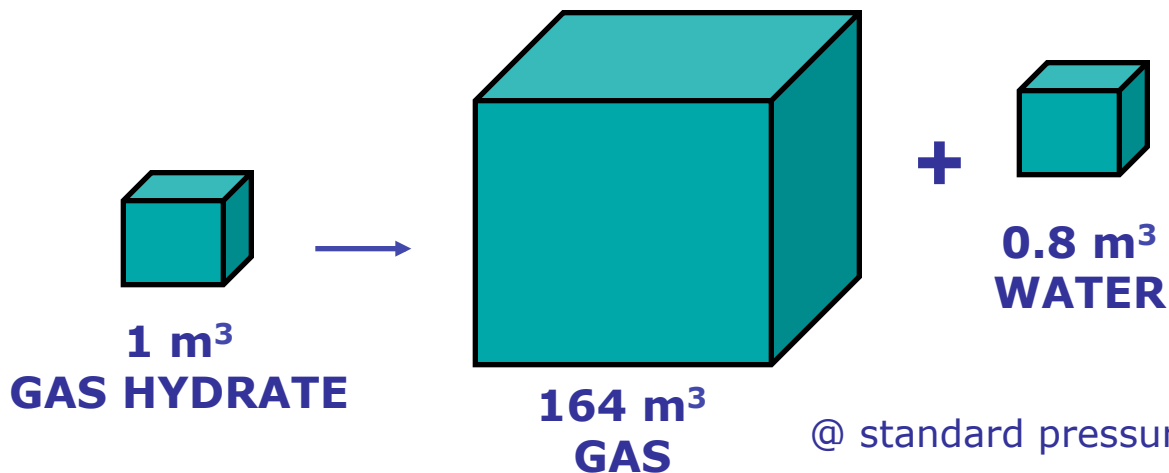


## Methane molecule

## Hydrate crystal



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



@ standard pressure and temperature



RCOM - University of Bremen

*Courtesy:*

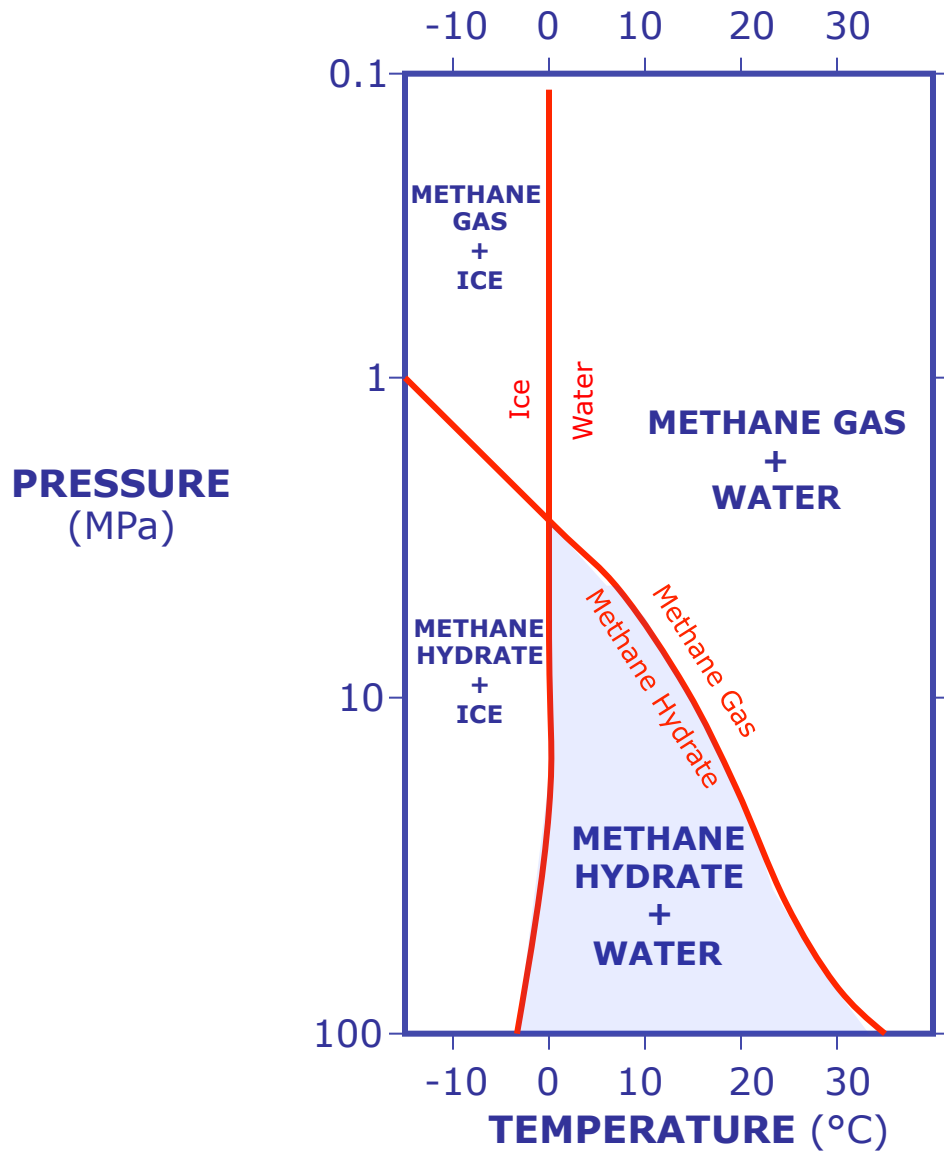
*Carlo Giavarini, Filippo  
Maccioni and Maria  
Laura Santarelli*

*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



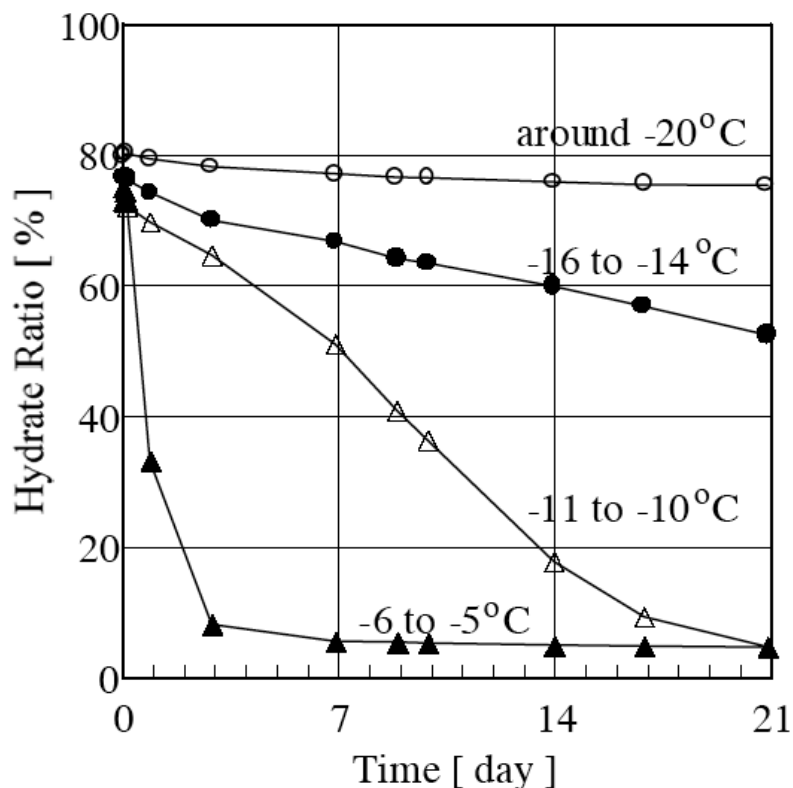
Methane is condensed into a liquid at almost atmospheric pressure (**Maximum Transport Pressure set around 25 kPa**) by cooling it to approximately  $-163^{\circ}\text{C}$ .

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



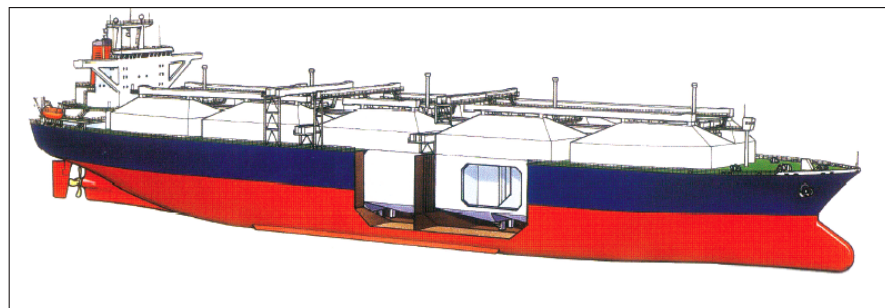
# self-preservation

At 1 Atm,  $\text{CH}_4$  Hydrates are stable below  $-20^\circ\text{C}$ .



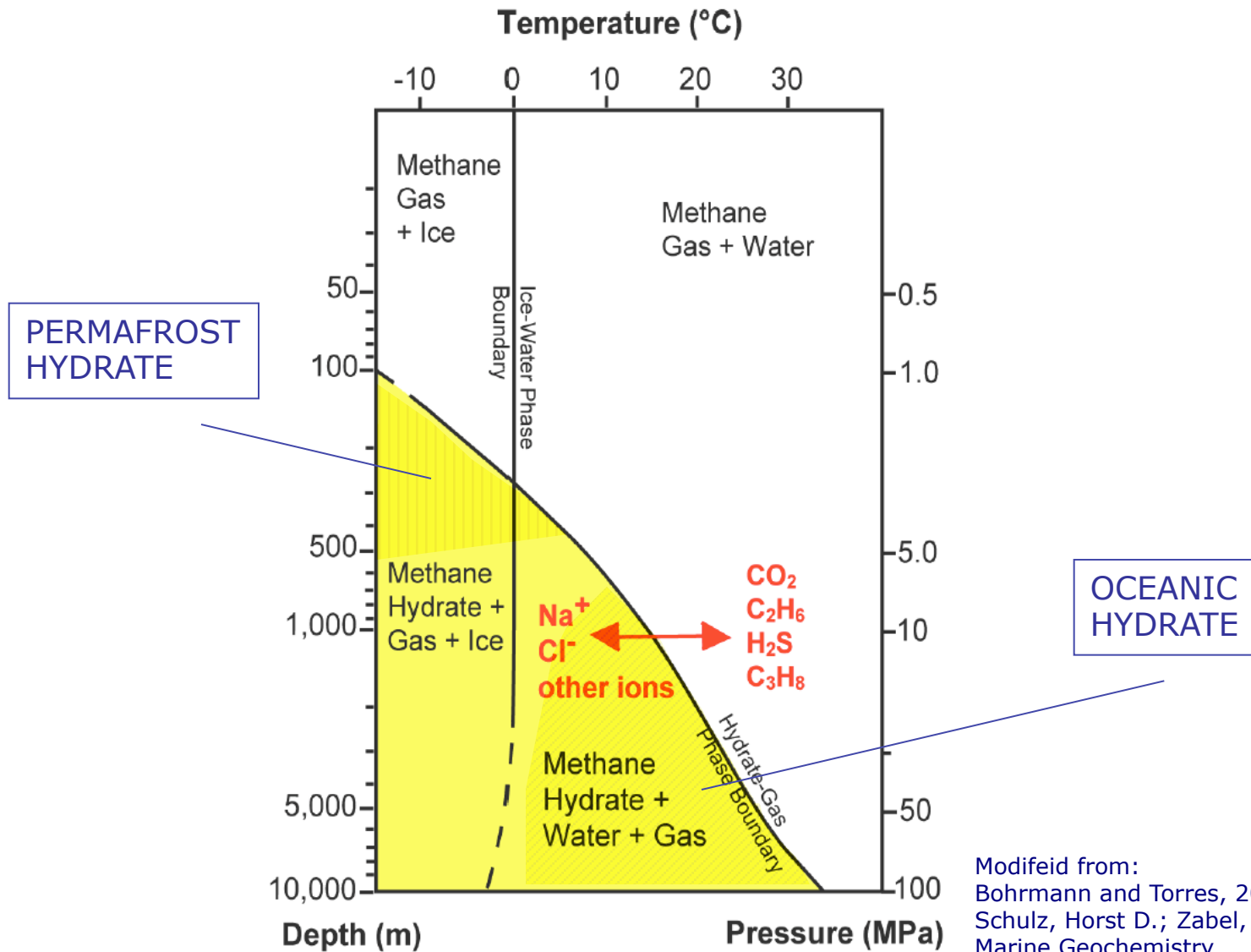
Self-preservation is thought to be caused by a layer of ice from dissociated hydrate; this layer coats the hydrate and seals it from further dissociation.

## Methane Hydrate Pellets



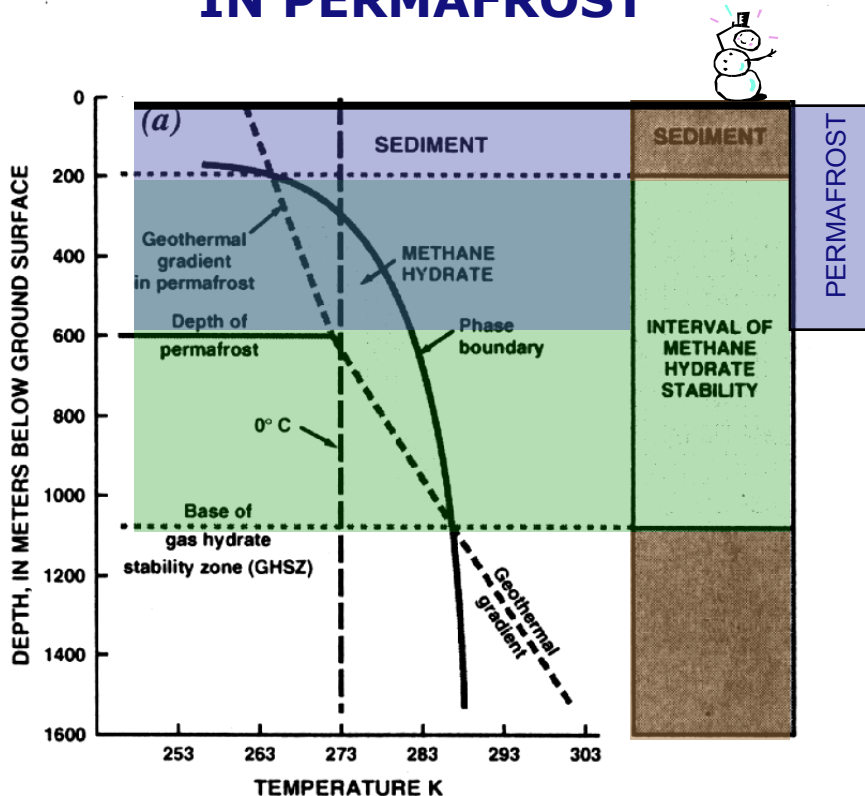
Possible ship specifically designed to carry natural gas **hydrate pellets** @  **$-20^\circ\text{C}$  and atmospheric pressure** (National Maritime Research Institute, Mitsui Shipbuilding & Engineering, and Osaka University)

# PHASE DIAGRAM OF METHANE HYDRATES IN THE NATURAL ENVIRONMENT



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

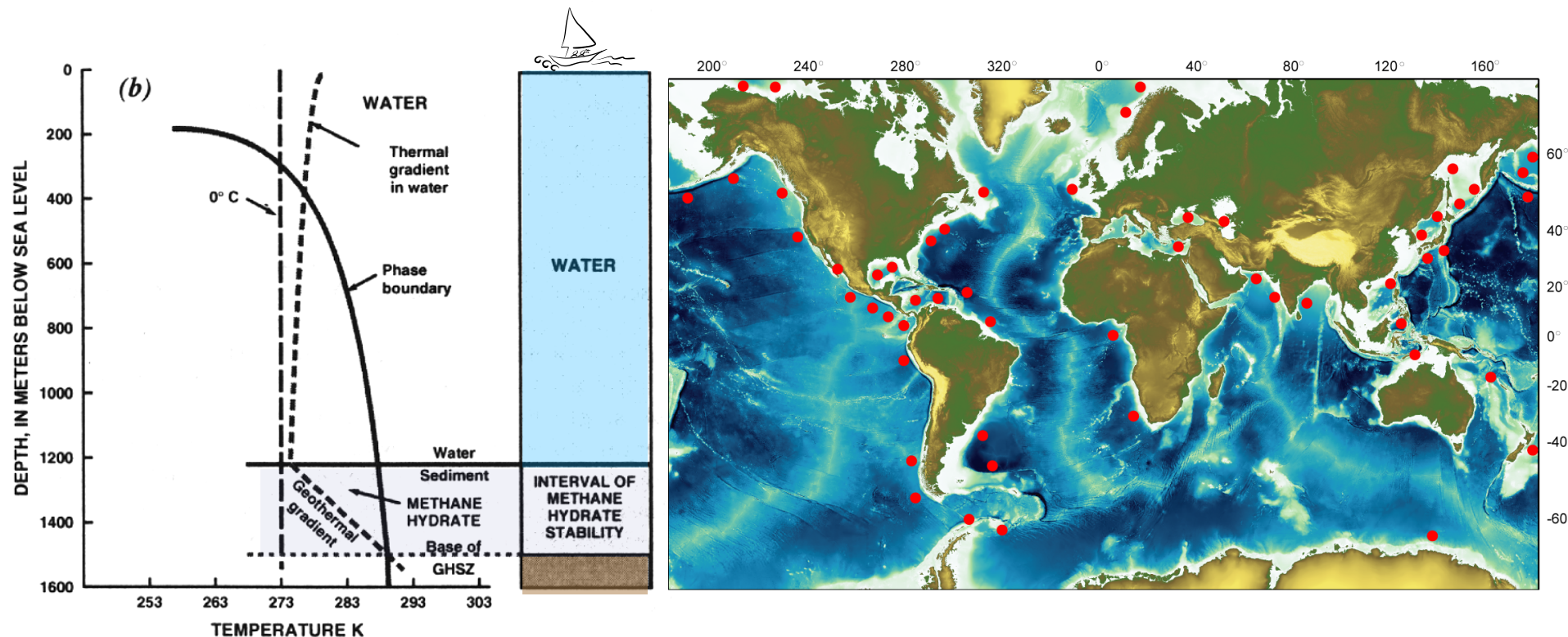
## METANE HYDRATES IN PERMAFROST



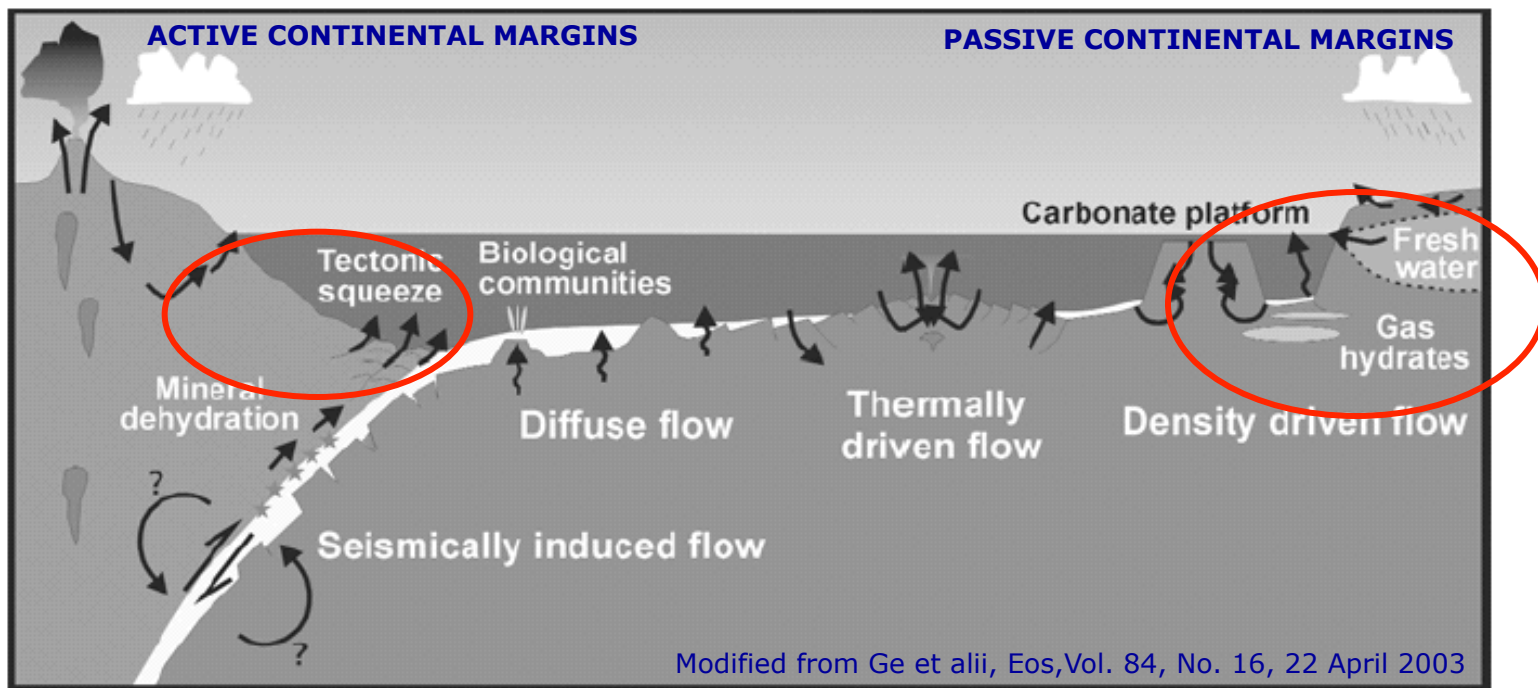
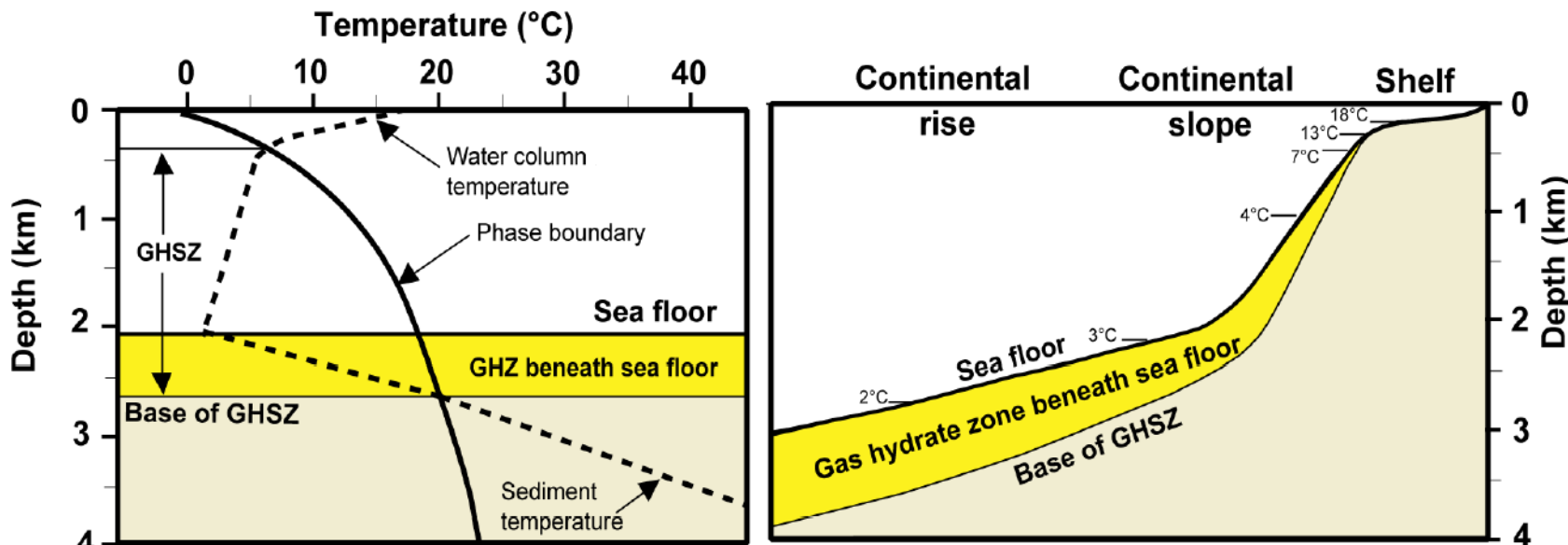
Source: International Permafrost Association, 1998. Circumpolar Active-Layer Permafrost System (CAPS), version 1.0.

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

# METHANE HYDRATES IN OCEANIC SEDIMENTS

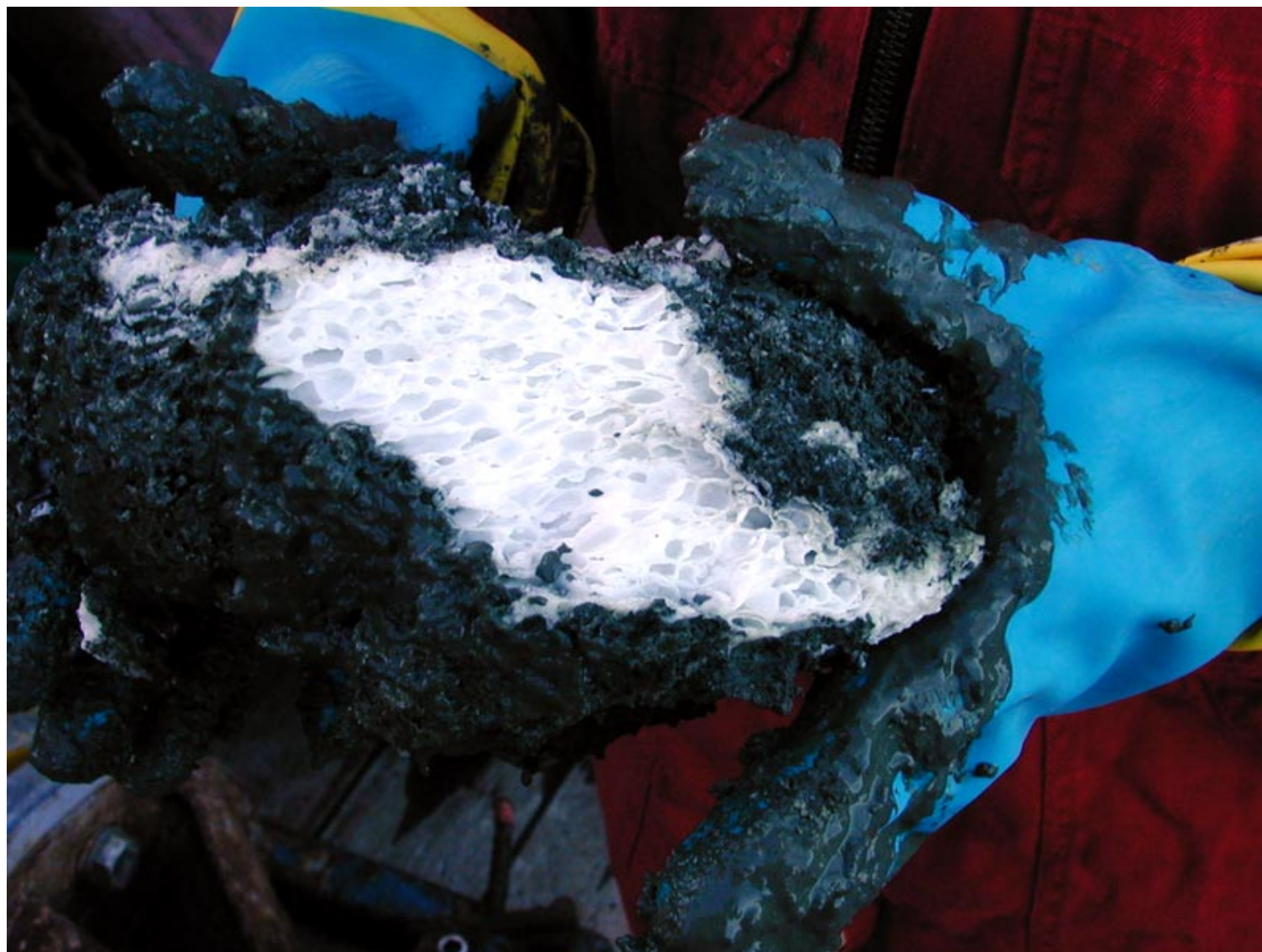


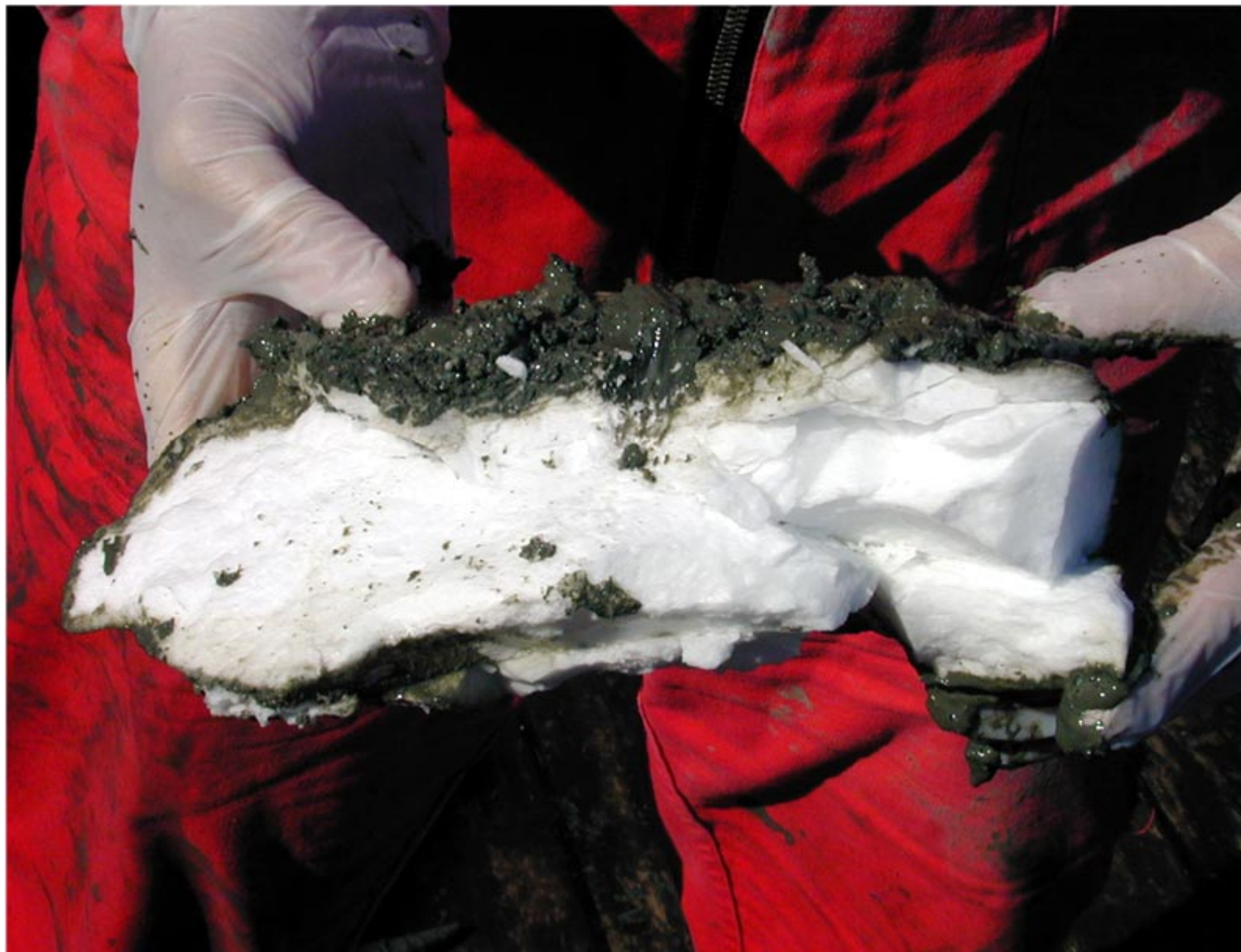
**Natural gas hydrates are distributed along the ocean margins world wide within the Gas Hydrate Stability Zone (GHSZ), that ranges from the seafloor down to a maximum of 700-800 m**

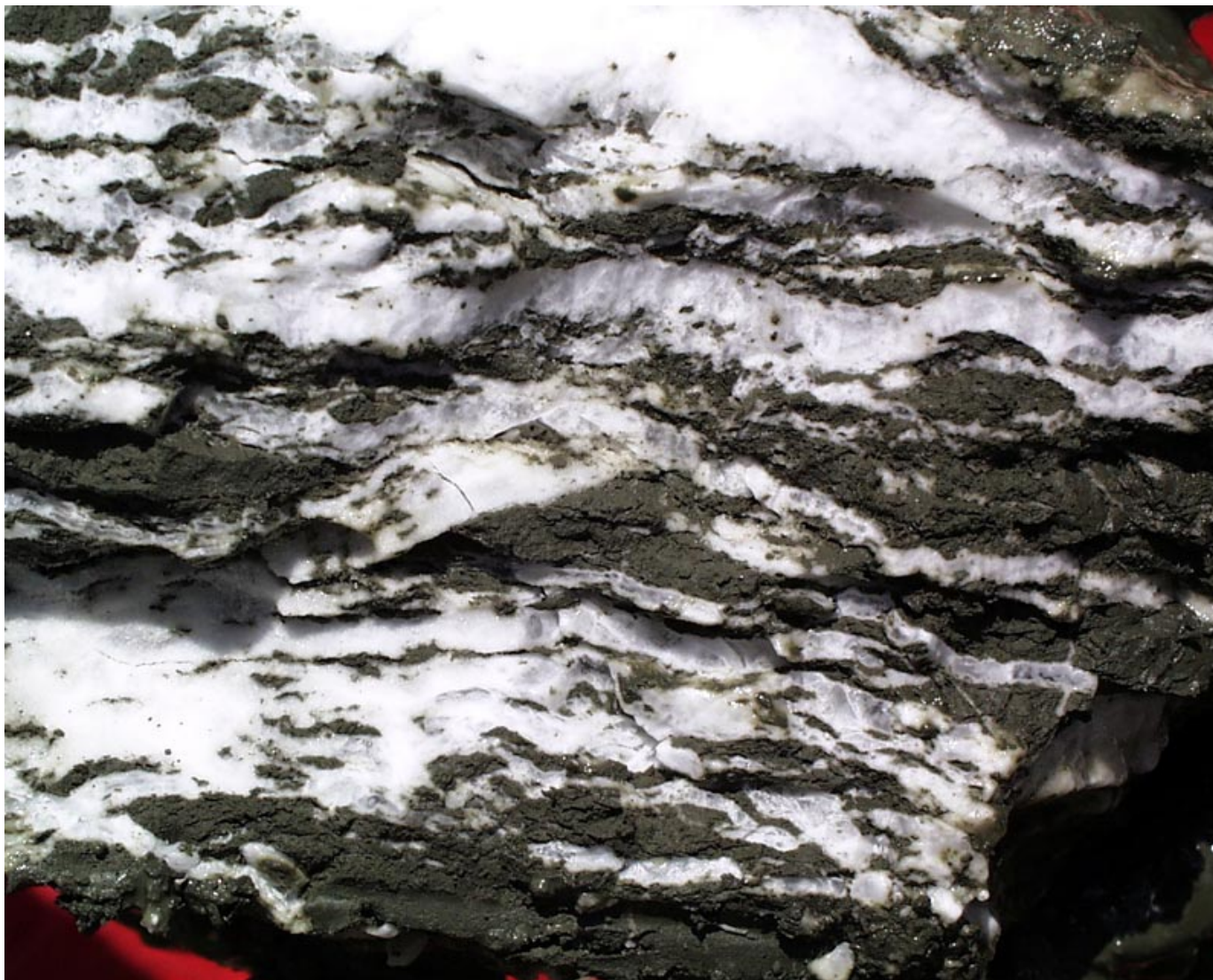


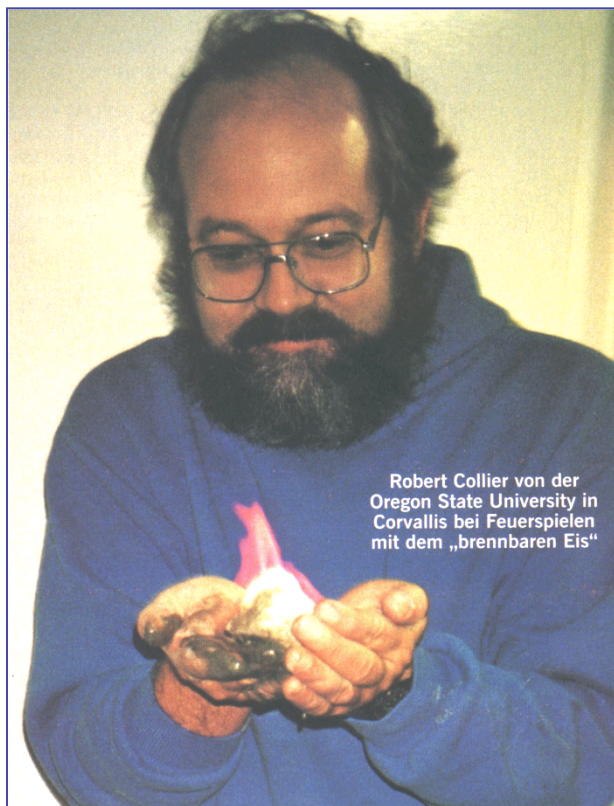




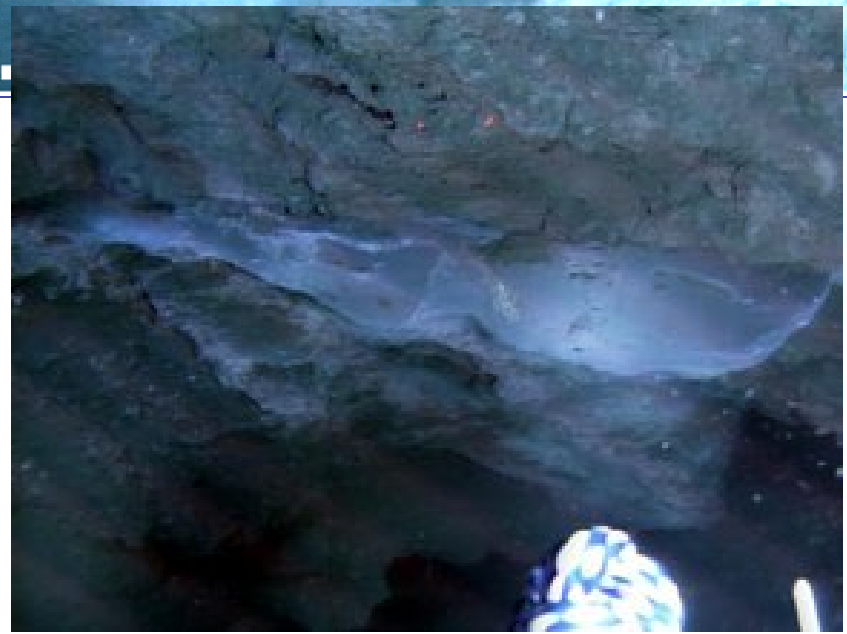
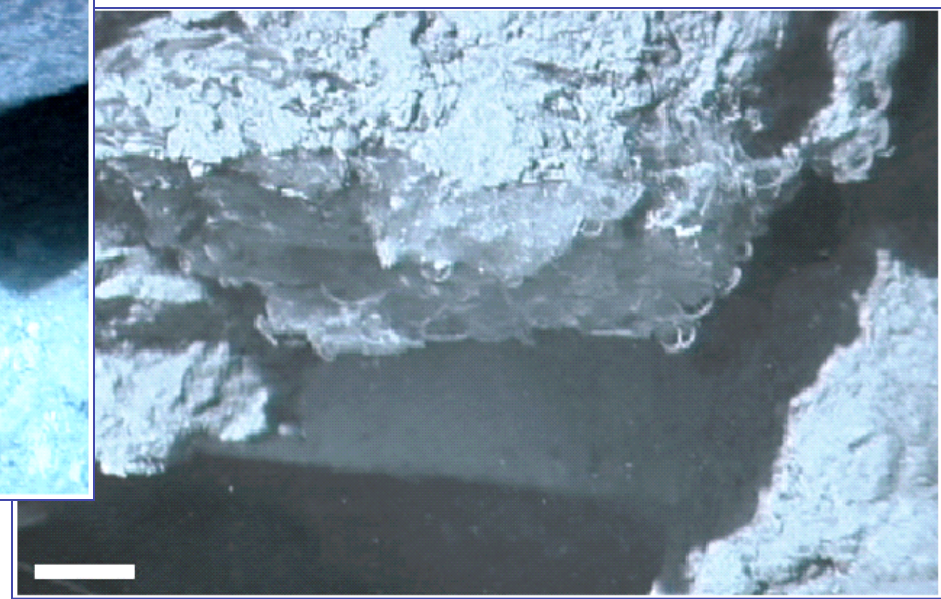
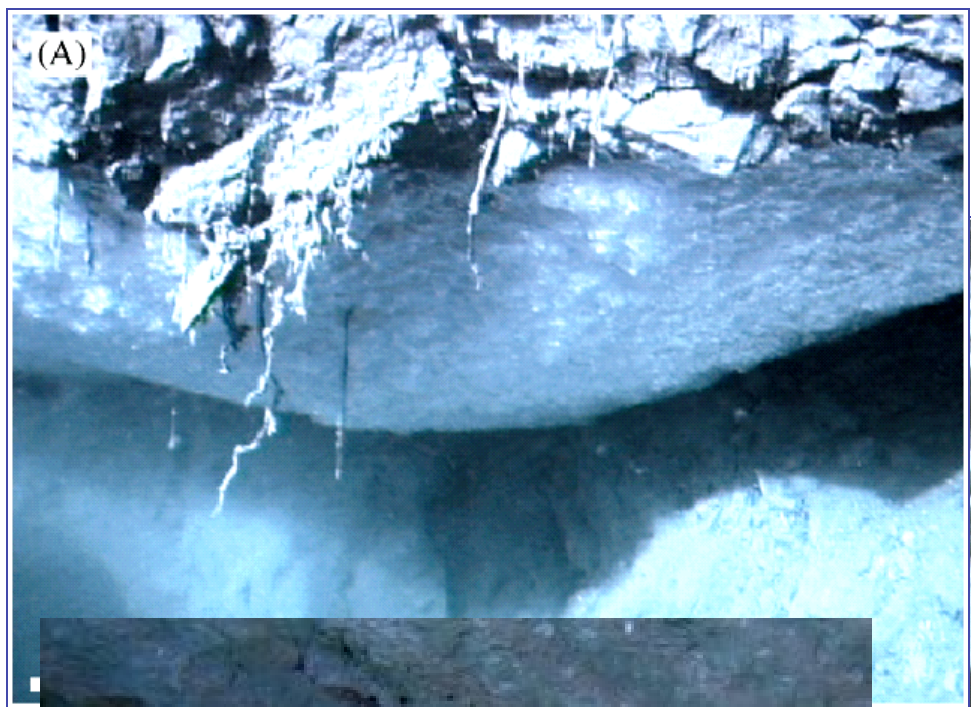










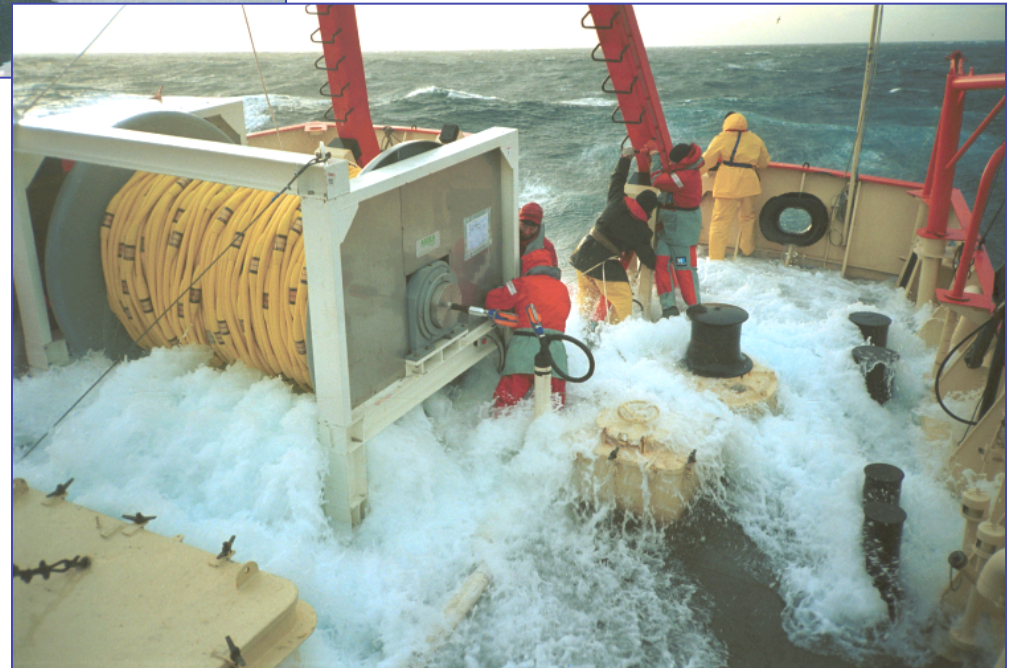


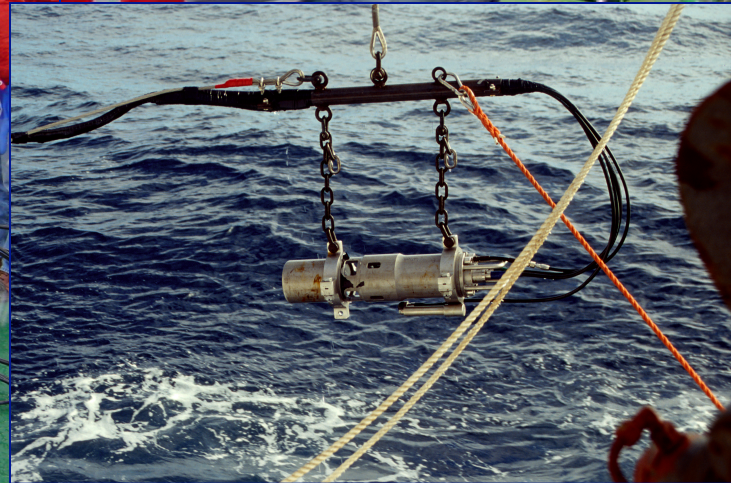
Van Dover et al. (2003). *Deep Sea Research*

# METHODS OF DETECTION OF NATURAL GAS HYDRATES

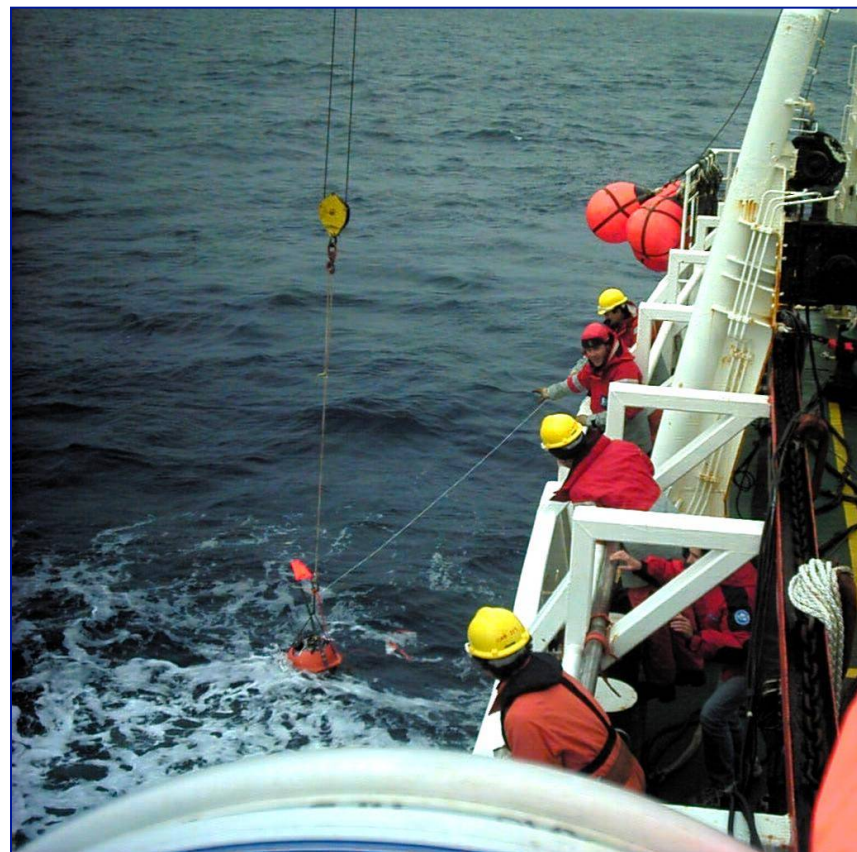
- **SEISMICS**  
(reflection, multichannel, OBS)
- **DRILLING**  
(essentially through scientific drilling)
- **GEOCHEMICAL**  
(inorganic- organic geochemistry)
- **MODELLING**  
(laboratory models - data inversion)
- **BASIN-WIDE ANALYSES**  
(modelling + data)







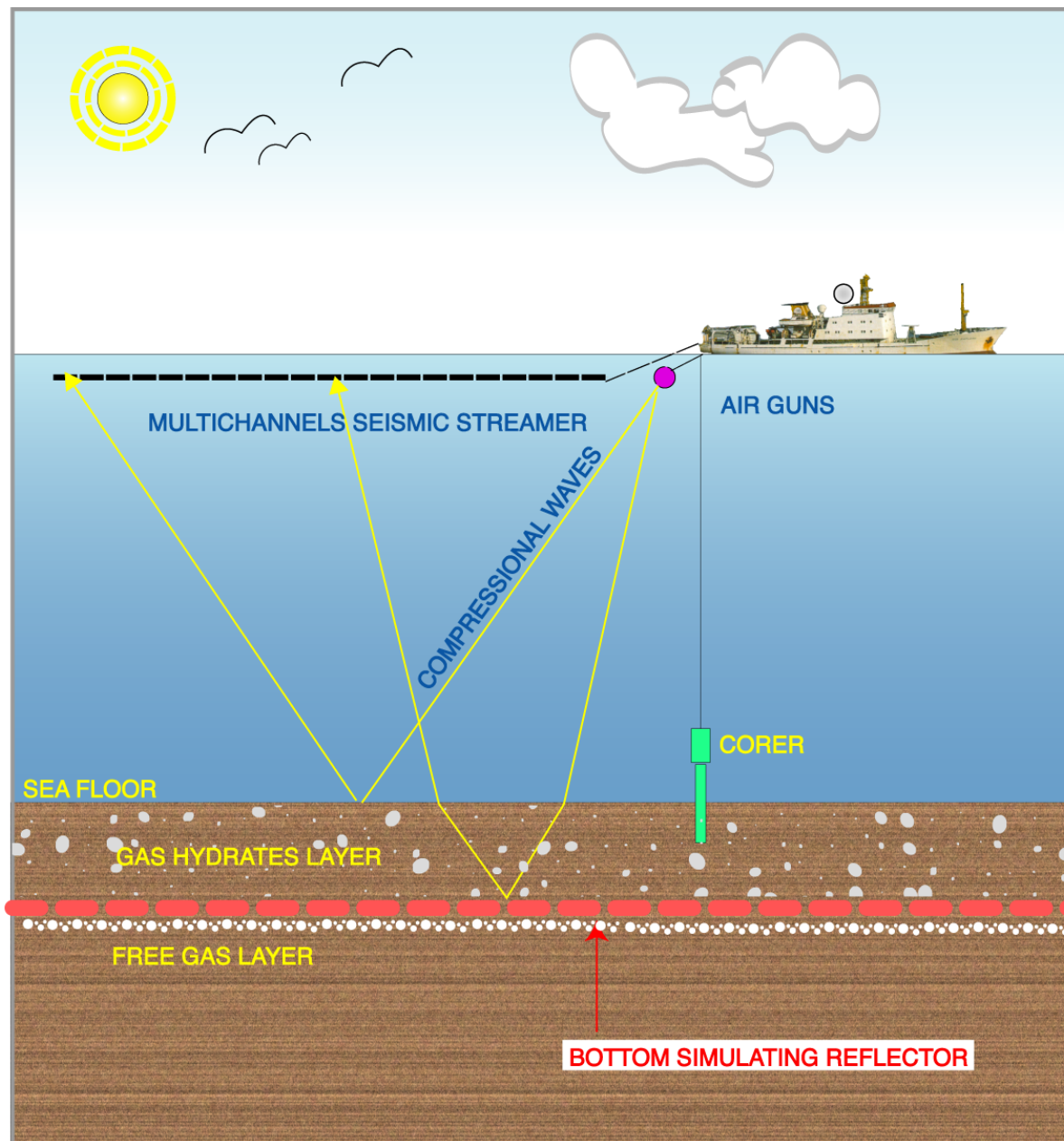
## OCEAN BOTTOM SEISMOMETERS (OBS)



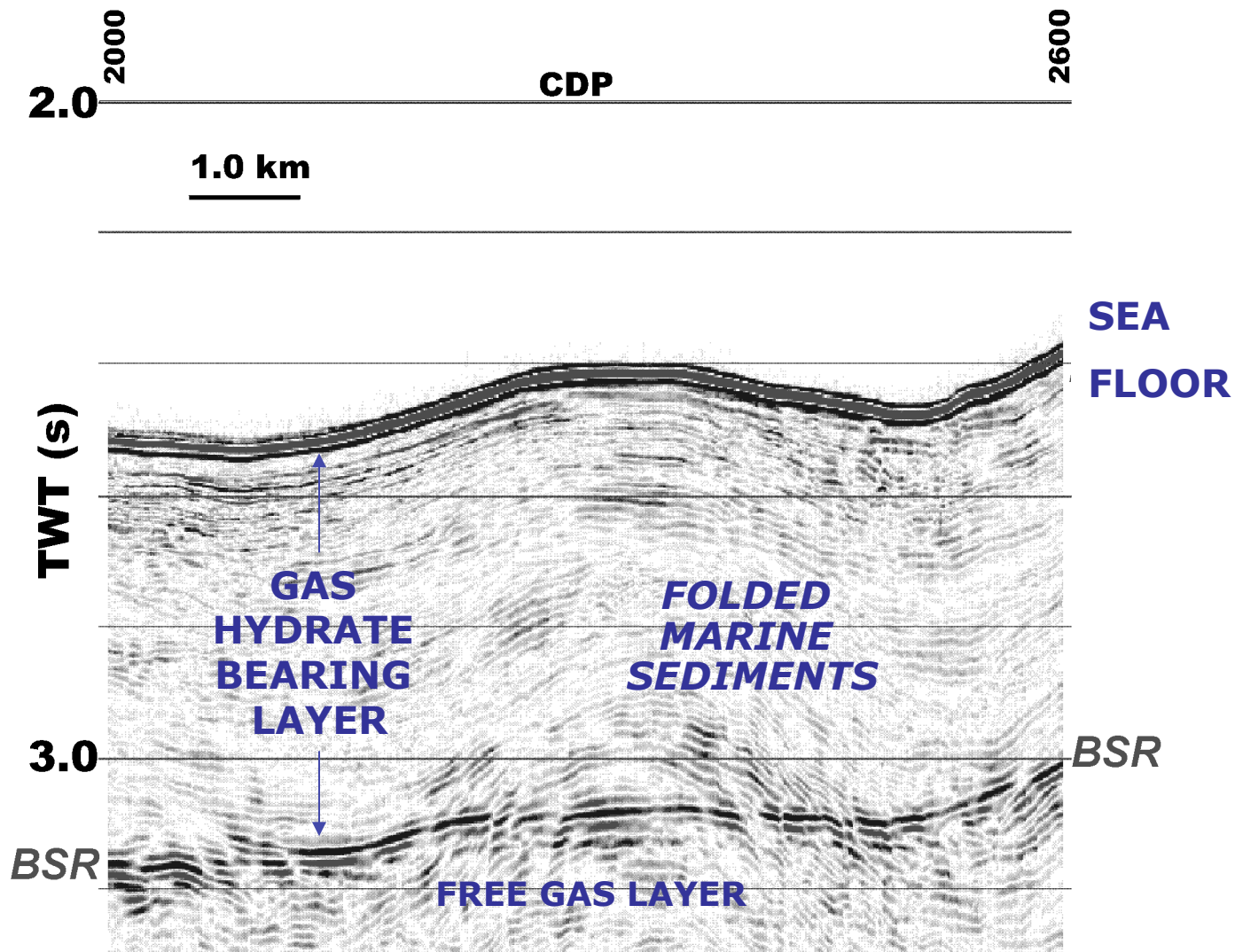
## SEISMICS REFLECTION

### 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).



# SEISMIC PROFILE



## Stratification in Marine Sediments

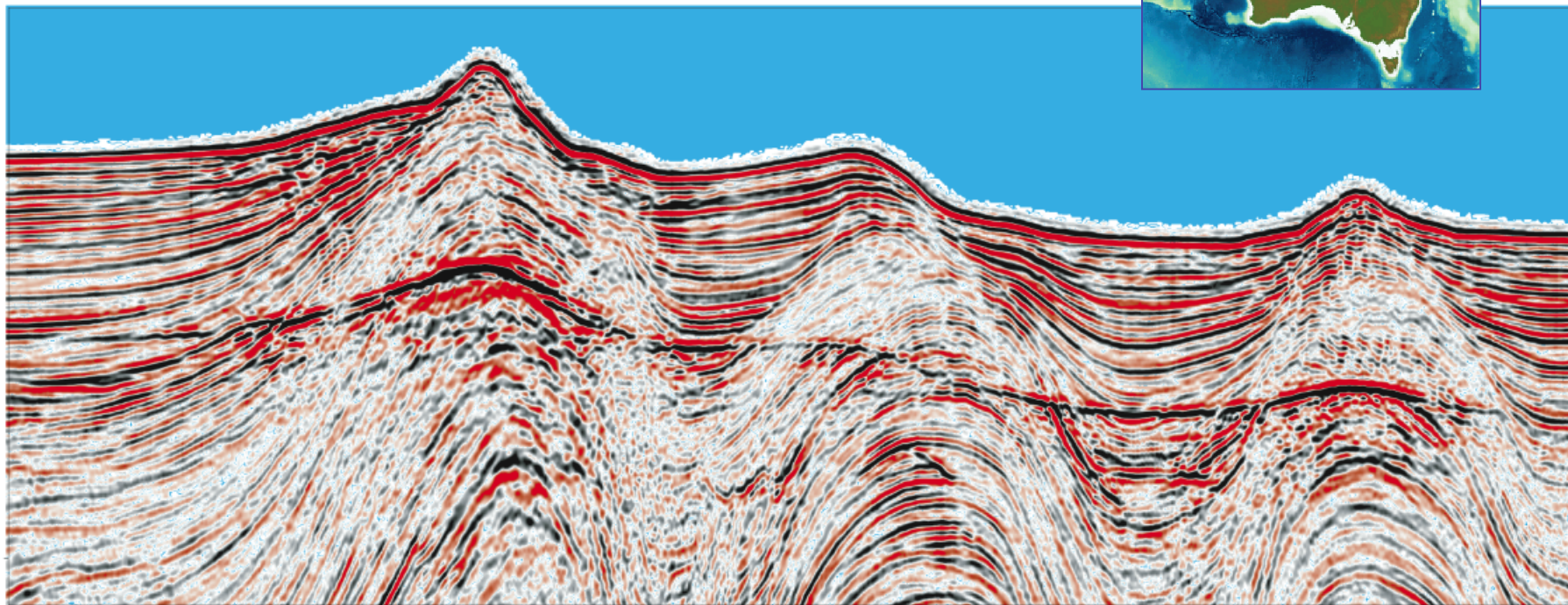


Turbidite (Gorgoglione Flysch),  
Miocene, South Italy



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



## Thermal anomaly in cores

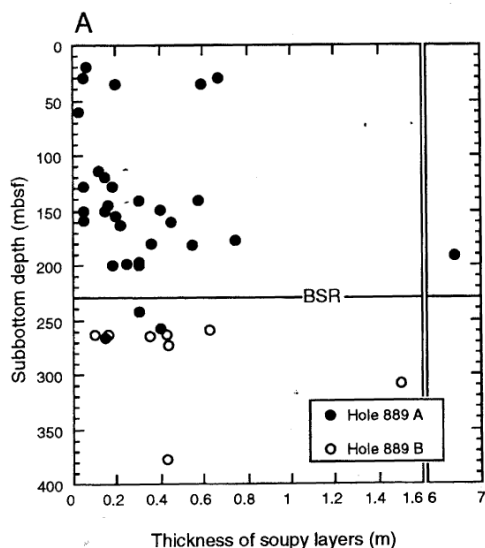


G. Bohrmann, Initial results from M52/1 **MARGASCH**

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

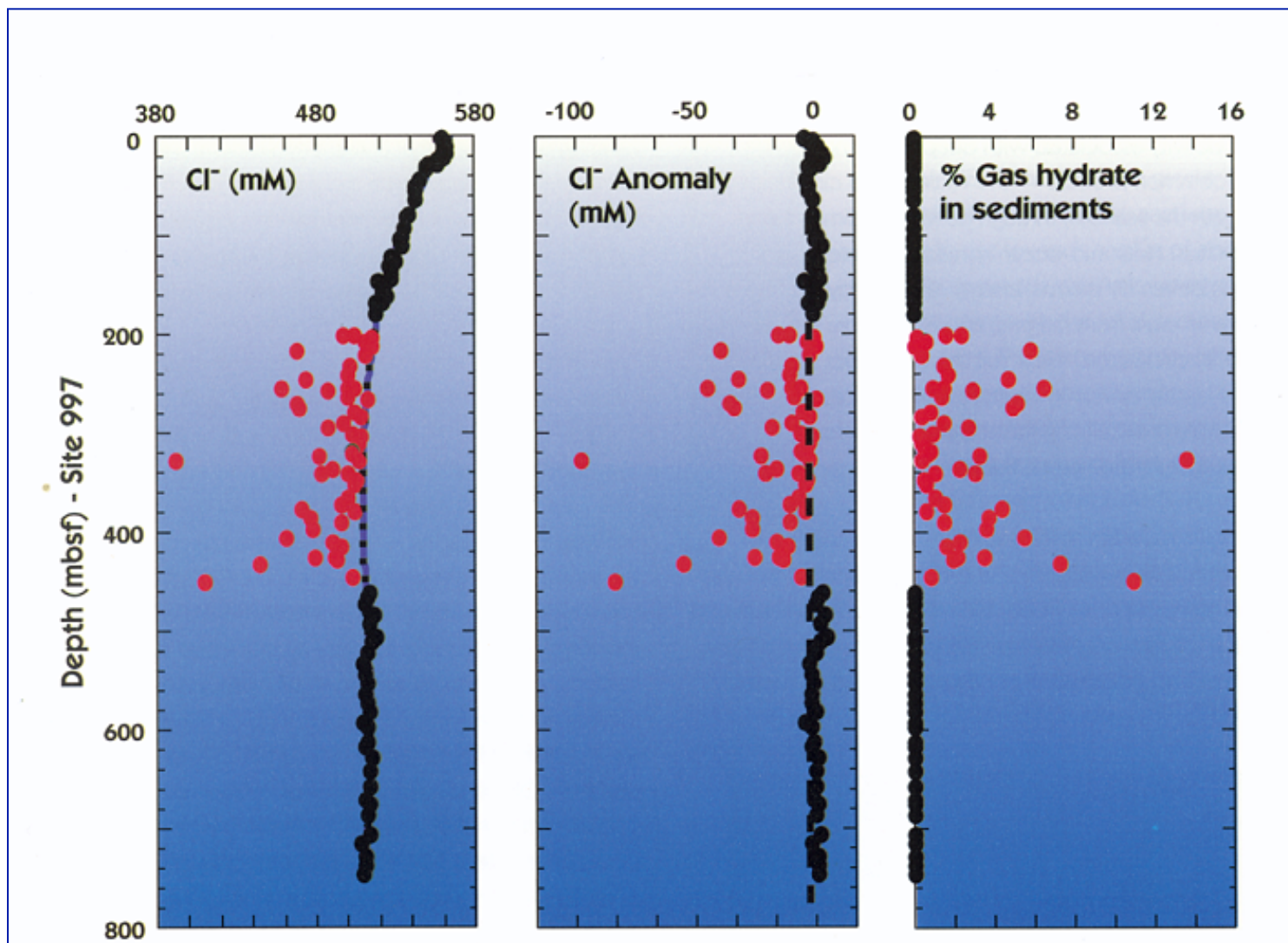


**SOUPY LAYERS: Sedimentological evidence of the presence of gas hydrates layers**



# Chlorinity anomaly

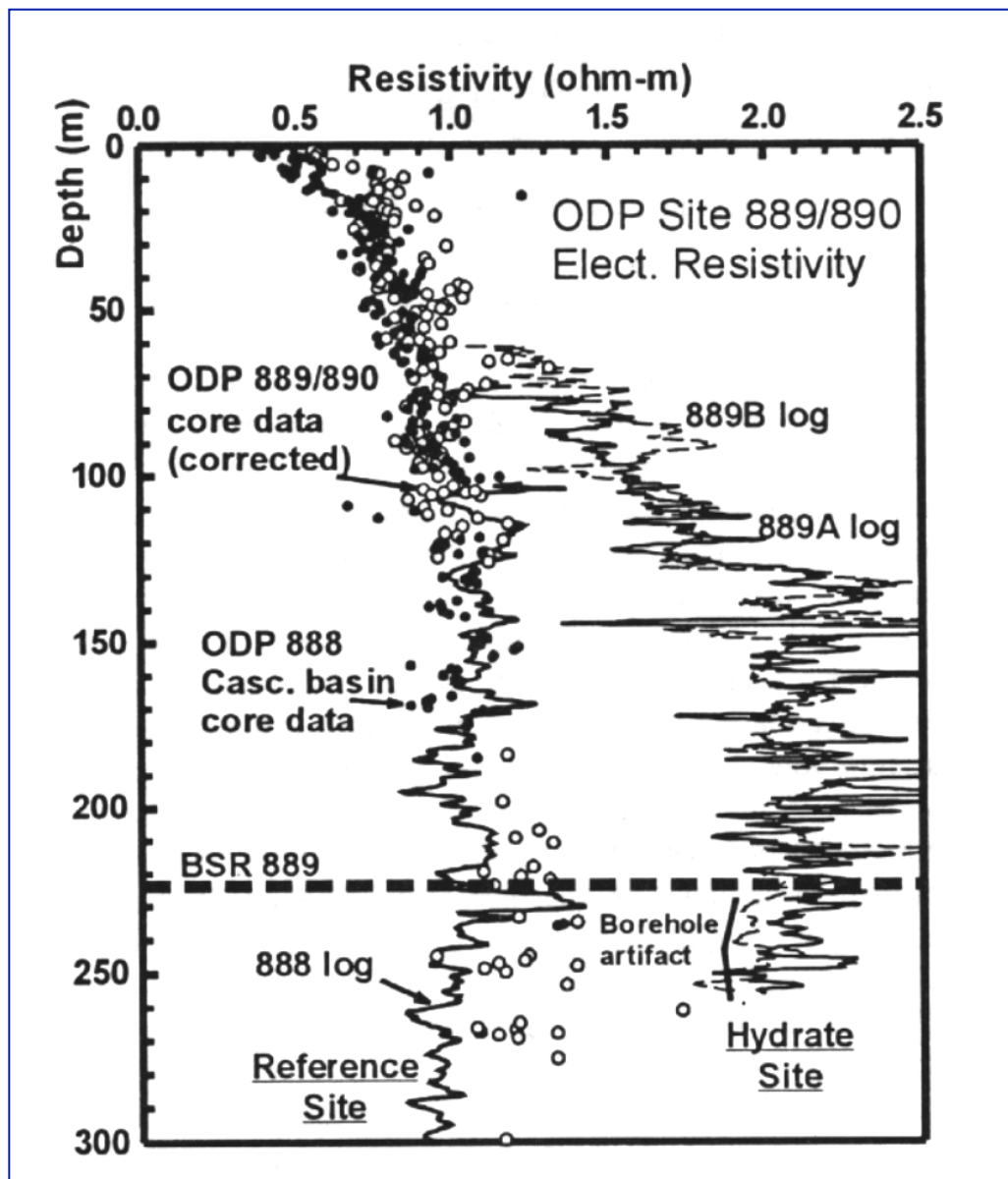
Gas hydrate dissociation during core recovery produces **residual fresh water** that dilutes the ionic concentration of the pore water



## *In situ* Electrical Resistivity anomaly

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

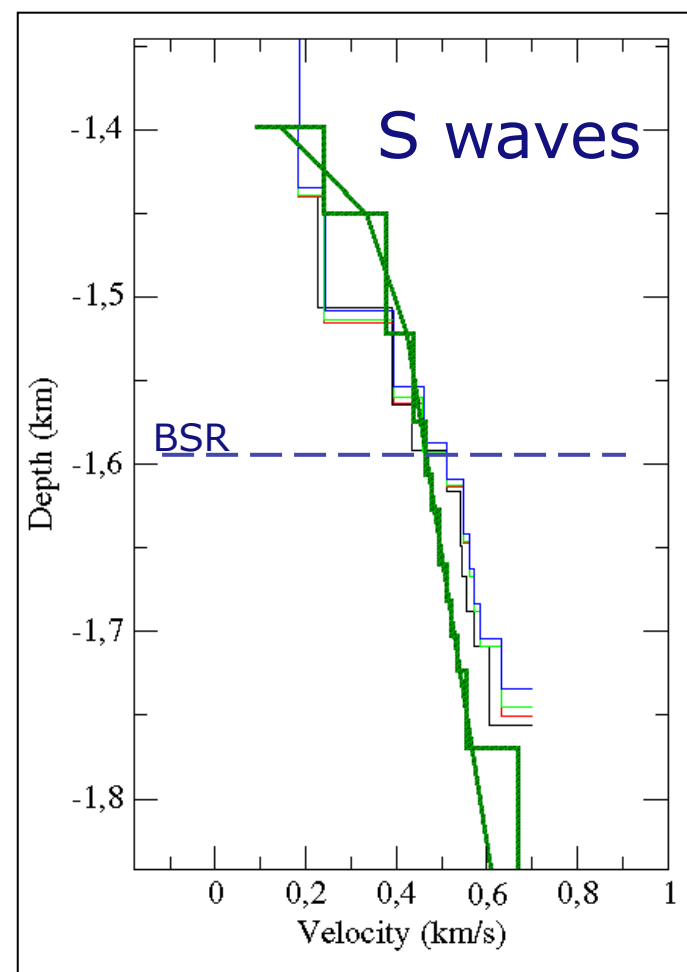
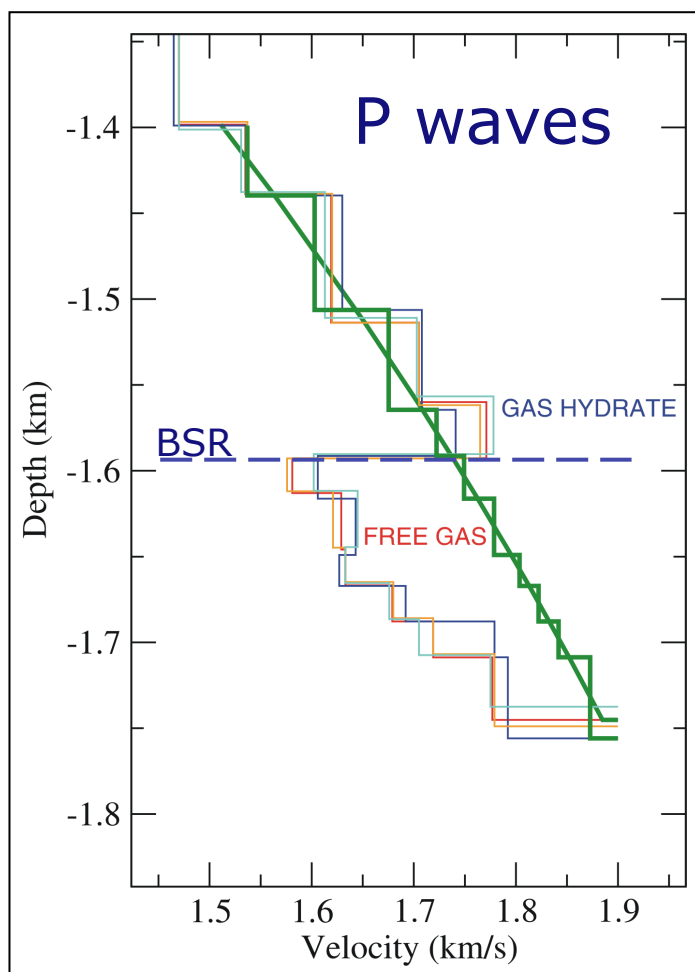
The anomaly is identified with respect to a resistivity profile in a nearby borehole with similar sediment NOT containing hydrates



# *In situ* seismic velocity anomaly

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

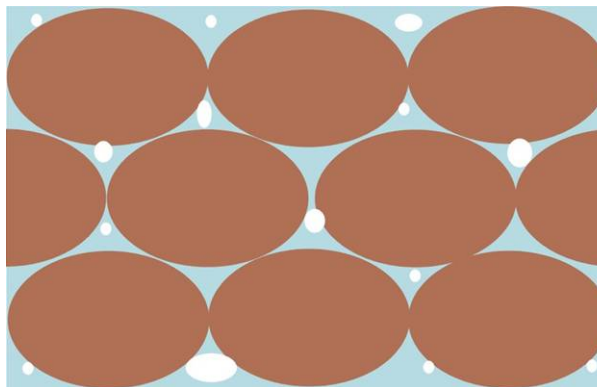
The anomaly is identified with respect to a resistivity profile in a nearby borehole with similar sediment NOT containing hydrates



## VELOCITY MODEL

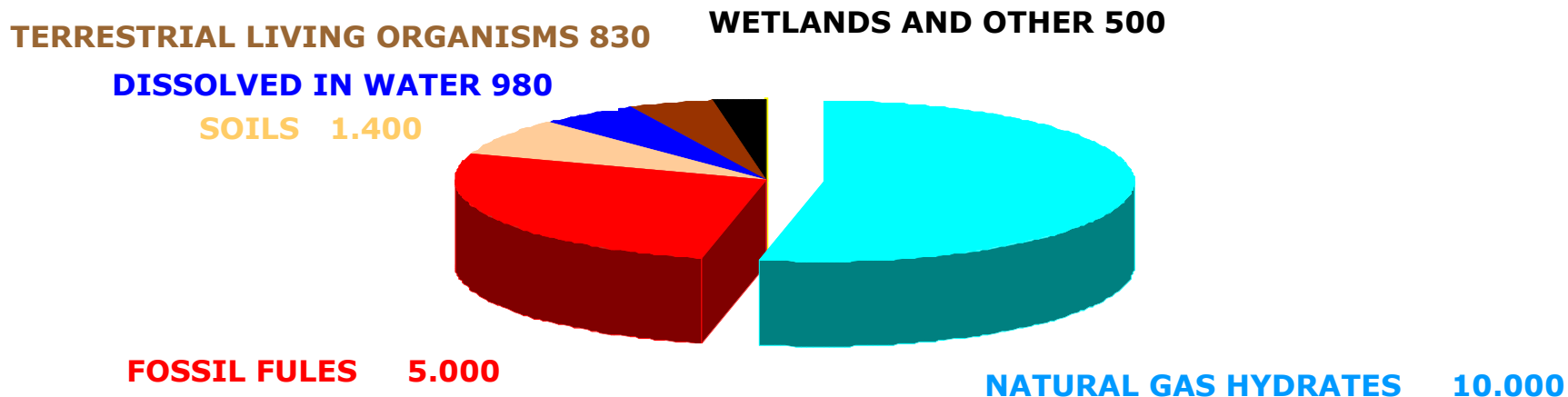
### *Biot-Geerstma-Smit equations*

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



# GLOBAL ESTIMATES

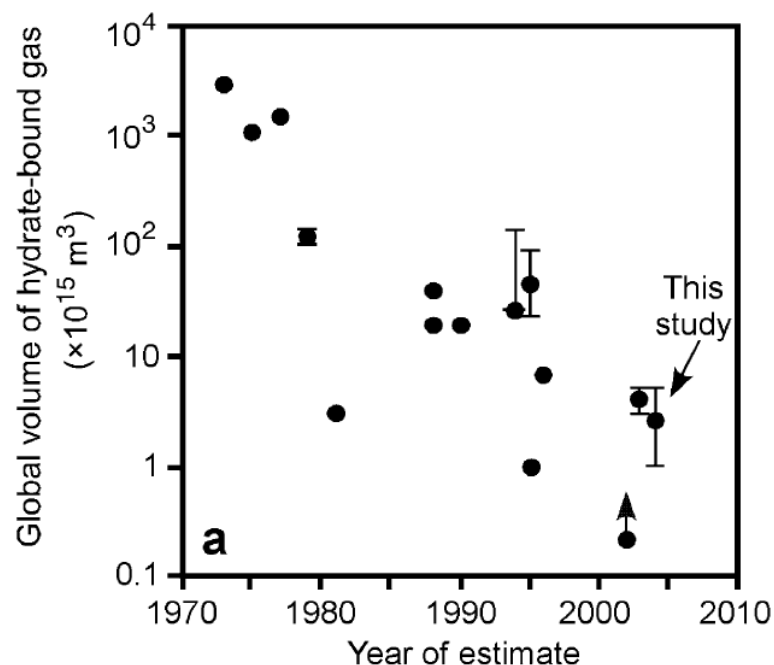
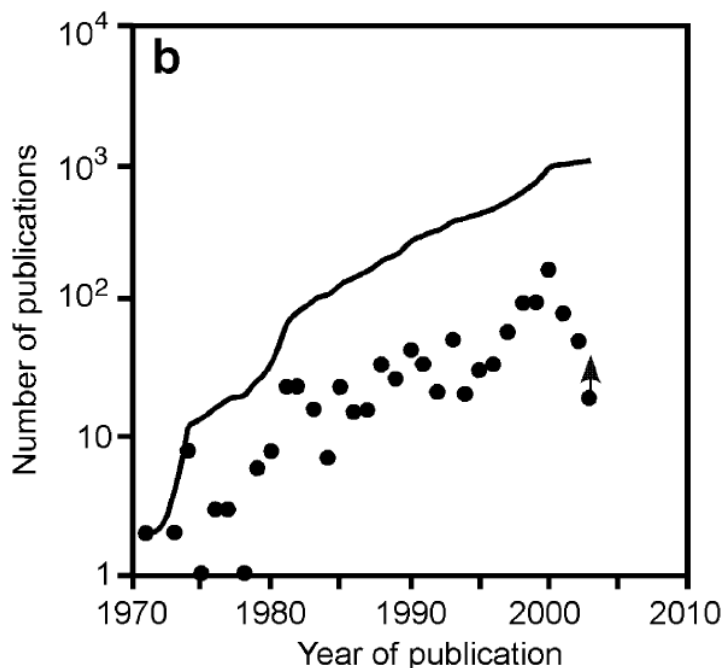
Estimation as amount of Carbon atoms ·  $10^{15}$  g





## HOWEVER.....

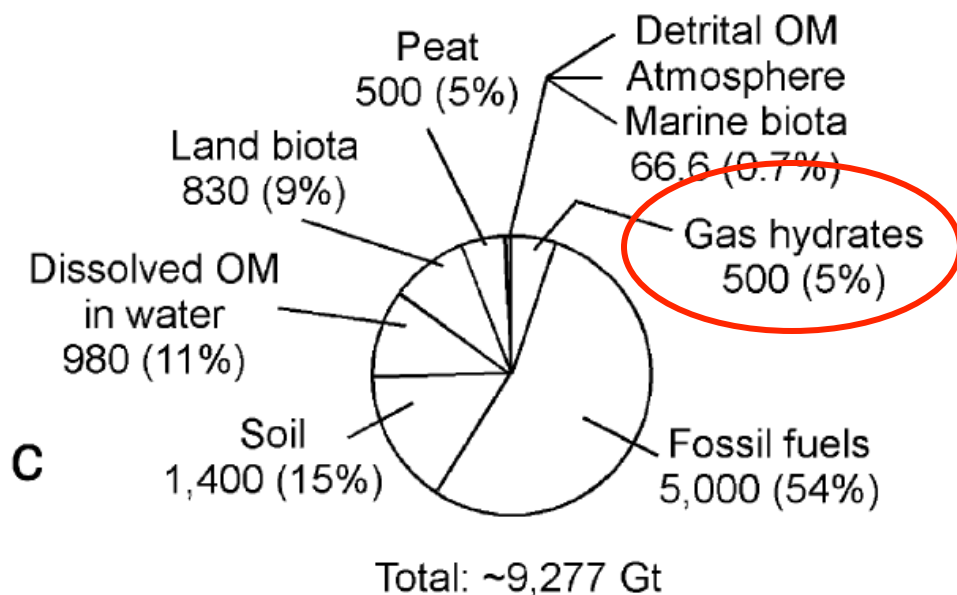
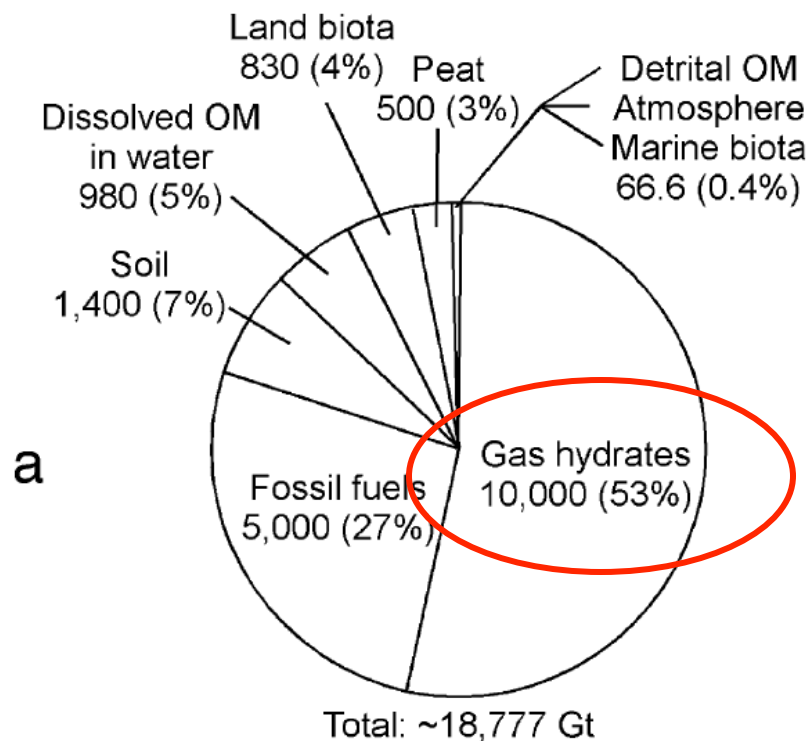
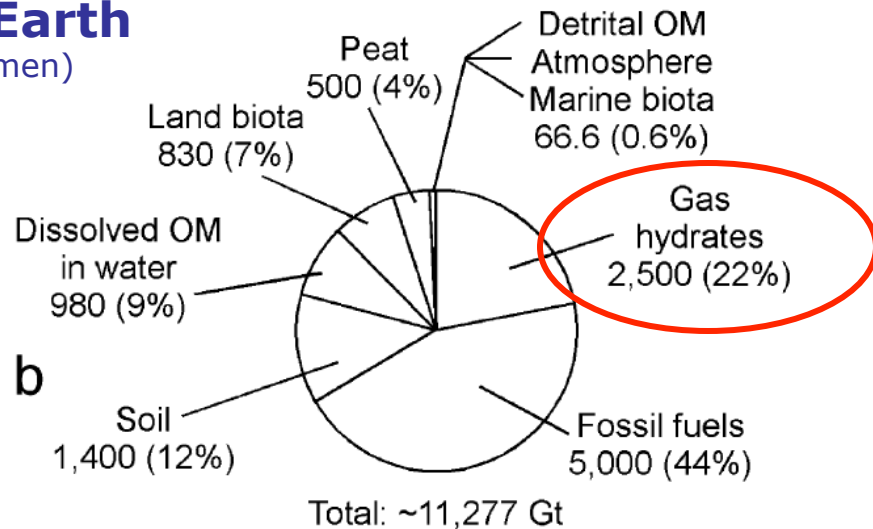
### Global estimates of the volume of hydrate-bound gas in marine sediments versus the year in which the estimate was made.



# 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.



## **In spite of changing global hydrates estimates.....**

- Methane is the cleanest fossil fuel:



- 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.

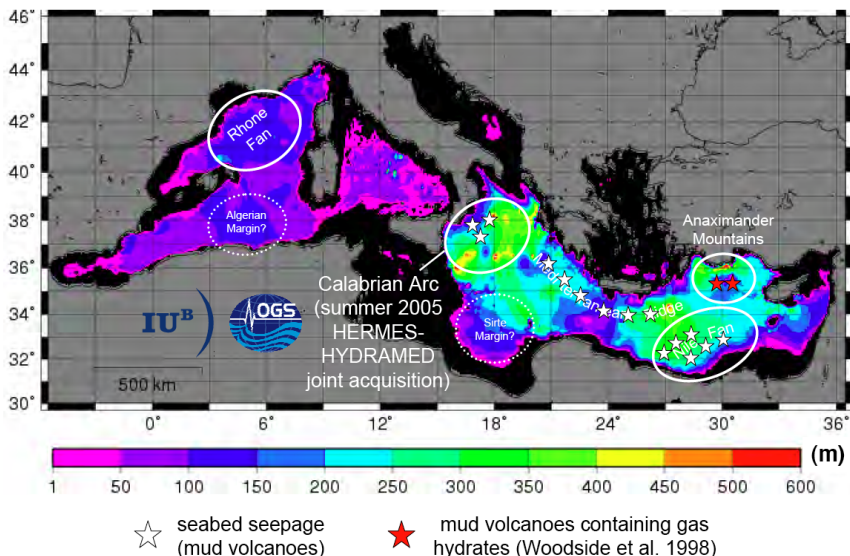
# Methane Hydrates are considered as NON CONVENTIONAL HYDROCARBONS by most oil companies

- 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 on 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 PROSPECTIVELY in the Mediterranean Sea

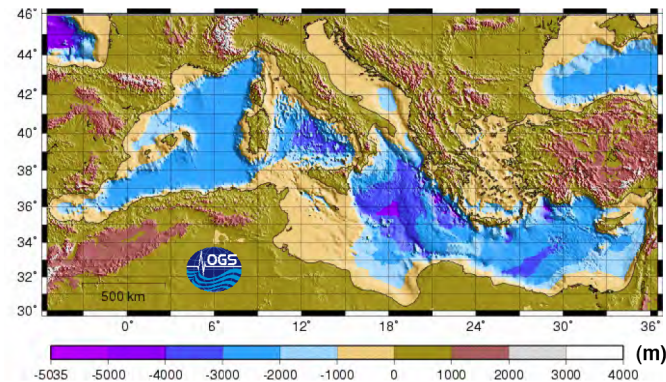


D. Praeg, V. Unnithan, and A. Camerlenghi, American Geophysical Unions Fall Meeting, December 2006

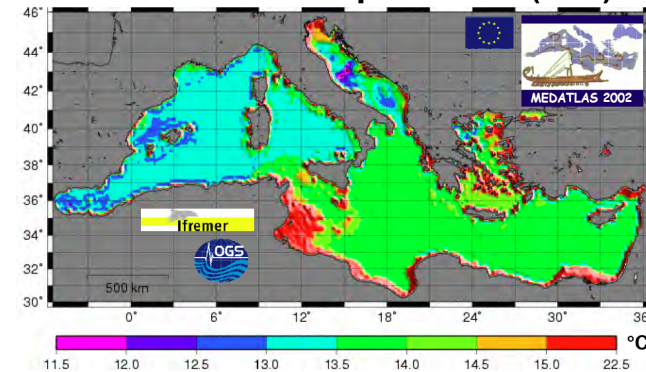
- Due to:
- High temperature of bottom water
  - High salinity of pore water
  - Presence of a salt seal (Messinian) preventing deep fluid migration

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

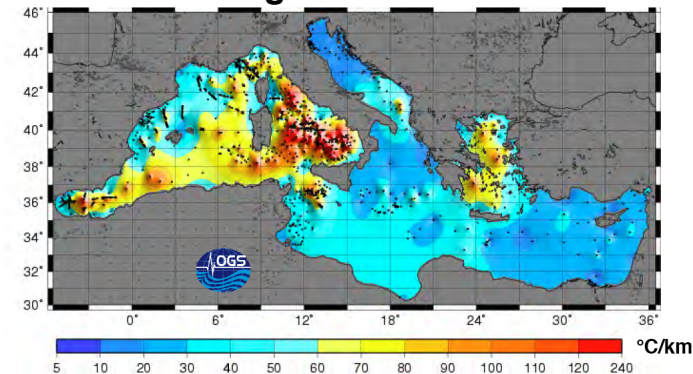
## Bathymetry



## Bottom water temperatures (bwt)



## Geothermal gradients

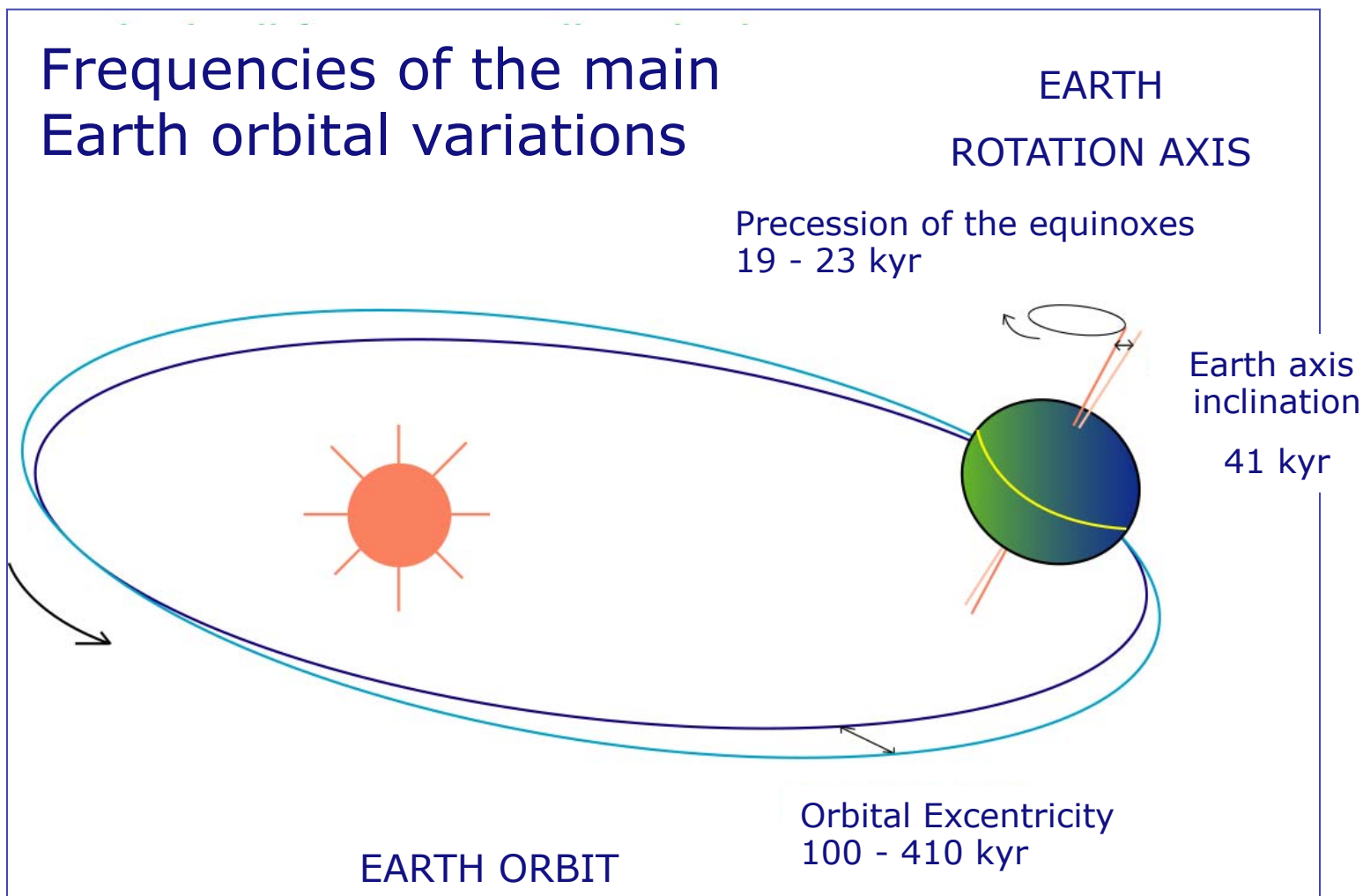


# METHANE HYDRATES AND GLOBAL CLIMATE



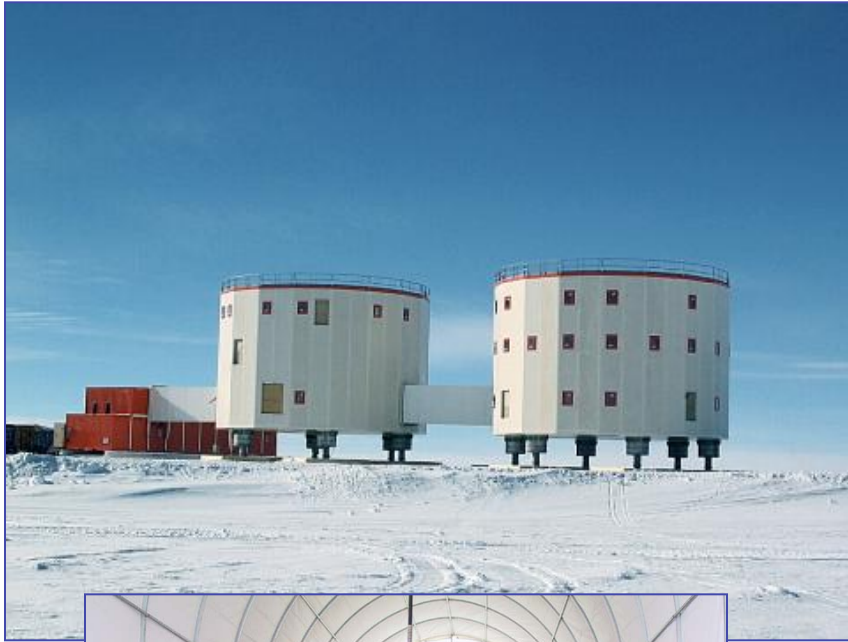
# MILANKOVITCH ORBITAL CYCLES

## Frequencies of the main Earth orbital variations

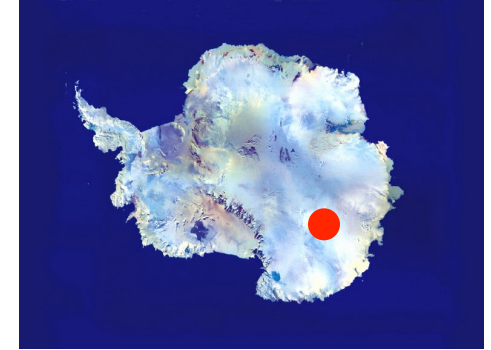


**The mean Solar radiation received by the earth changes through time. Such changes are the primary cause of glacial interglacial epochs and other climatic stages.**





Programma Nazionale di Ricerche in Antartide (PNRA)



Dome-C Station, Antarctica



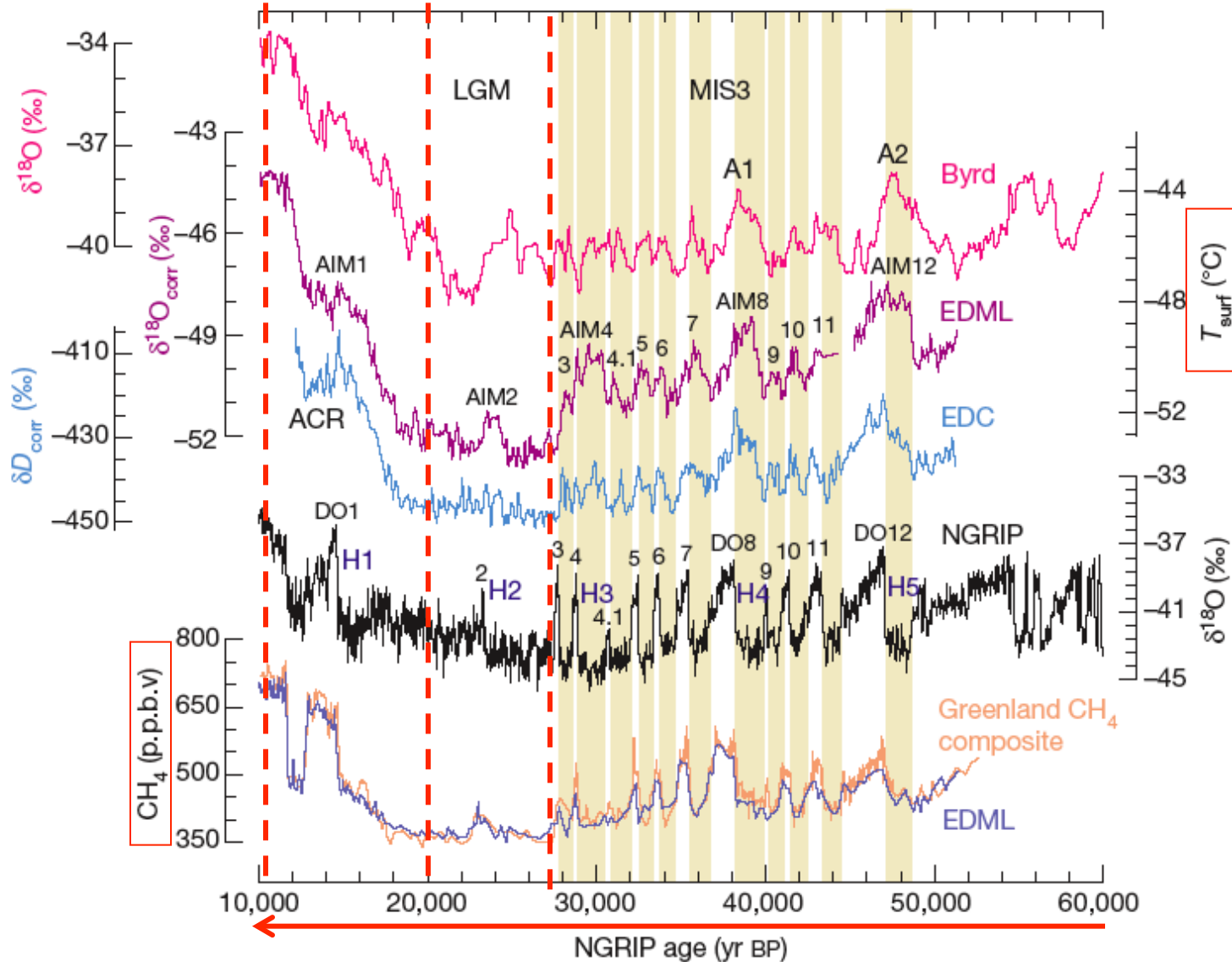
European Project for Ice Coring in Antarctica (EPICA)

PRESENT INTERGLACIAL  
(HOLOCENE)

DE-  
GLACIATION

LAST GLACIAL  
MAXIMUM

GLACIAL



PALEO-TEMPERATURE INDICATORS

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

## **IN MARINE SEDIMENTS:**

- WHEN OCEAN BOTTOM WATER TEMPERATURE RISES (DEGLACIATION) SOME METHANE CHANGES FROM HYDRATE FORM TO GASE FORM AND ESCAPES FROM THE 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 TAKEN INTO ACCOUNT.

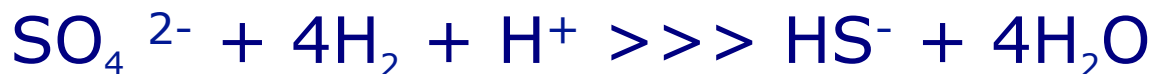
## Anaerobic oxidation of methane (AOM) via sulfate reduction.

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

The archaea oxidize methane:



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



## Authigenic carbonate precipitation Methane-derived Calcium Carbonate.

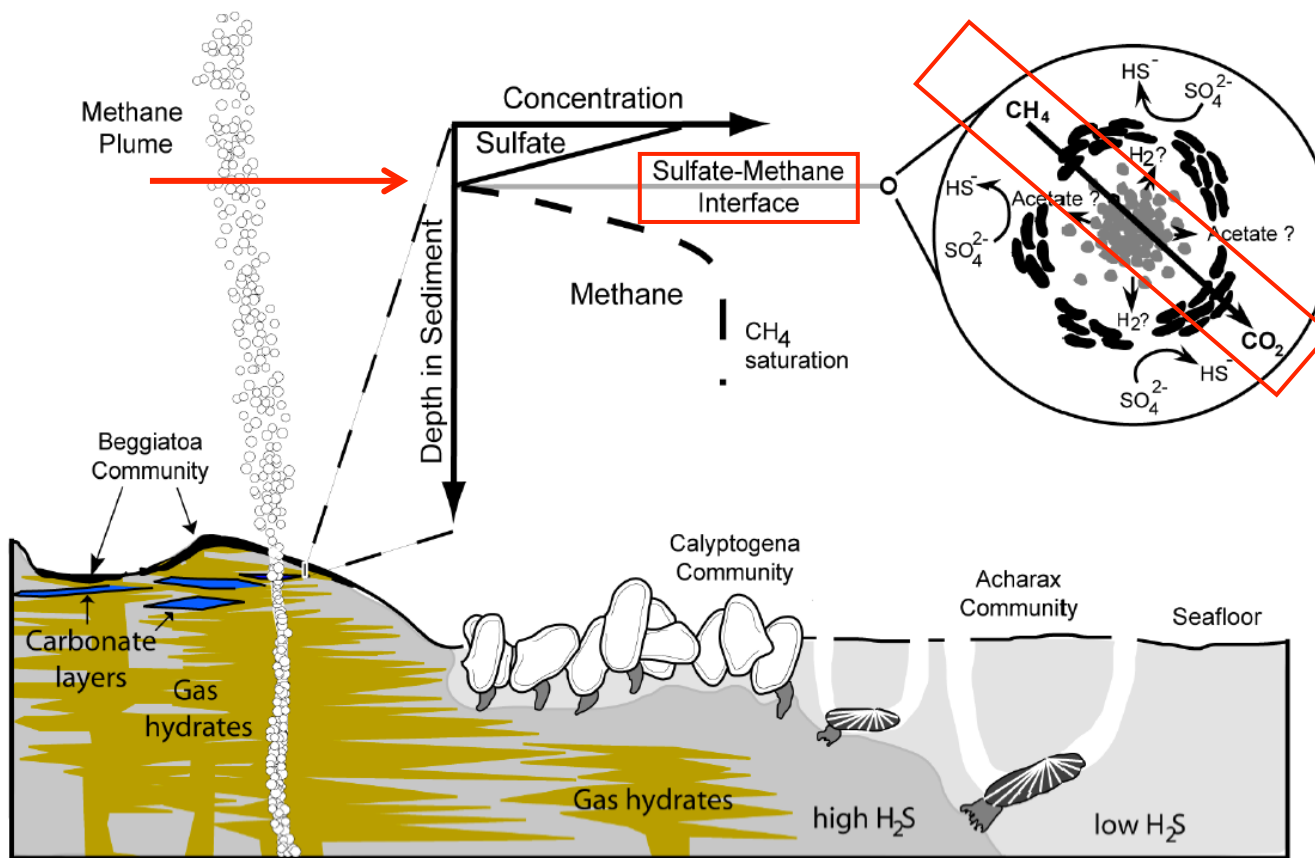


Bicarbonate  
from bacterial action

alkaline  
seawater

calcium ions  
present in seawater

calcium  
carbonate deposited



Bathymodiolus heckeriae 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 ( $\text{CaCO}_3$ )**



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

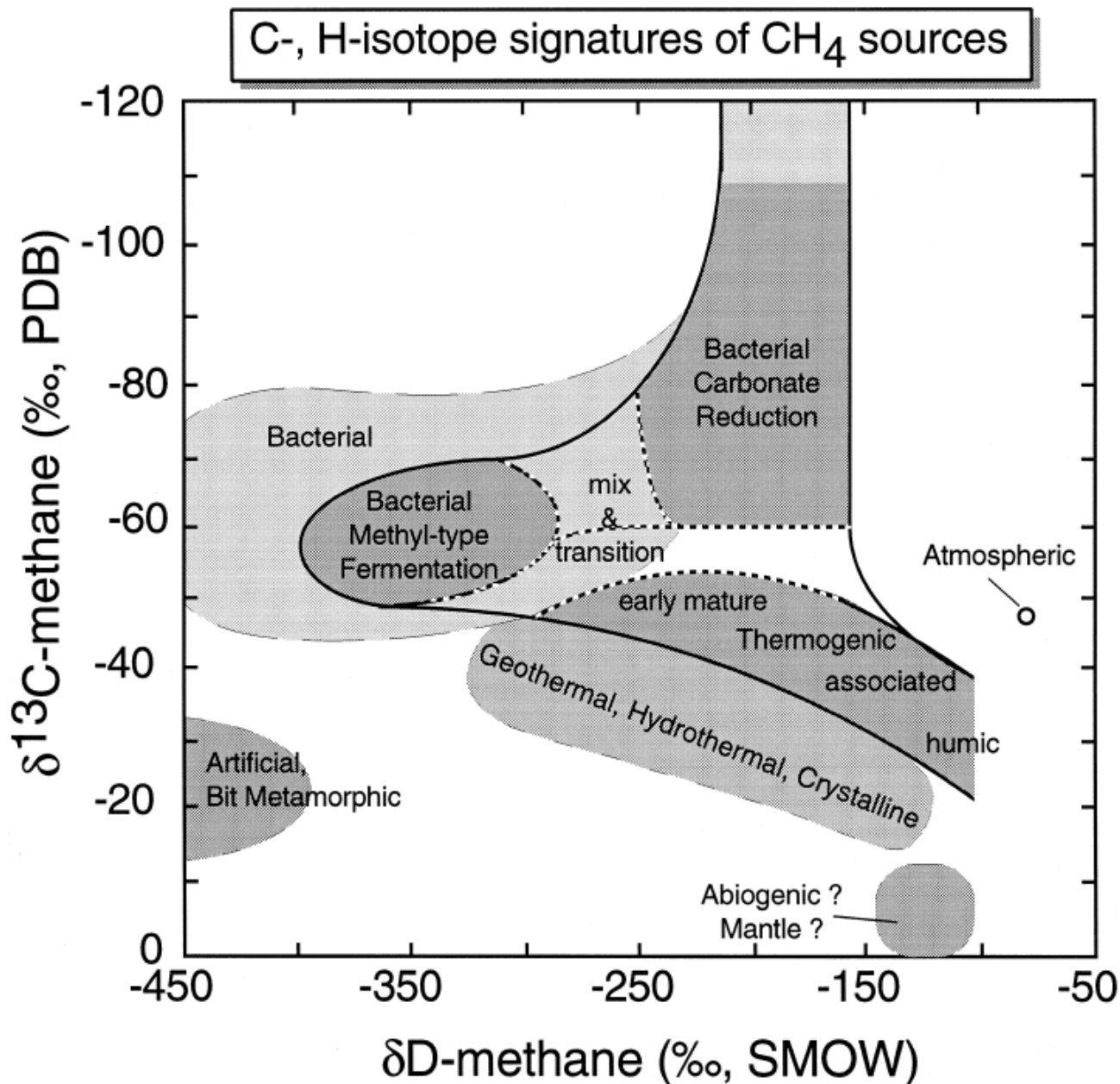
**Normal marine environment:  $\delta^{13}\text{C}_{\text{DIC}} \cong 0\text{‰}$**

(Peterson e Fry, 1987)

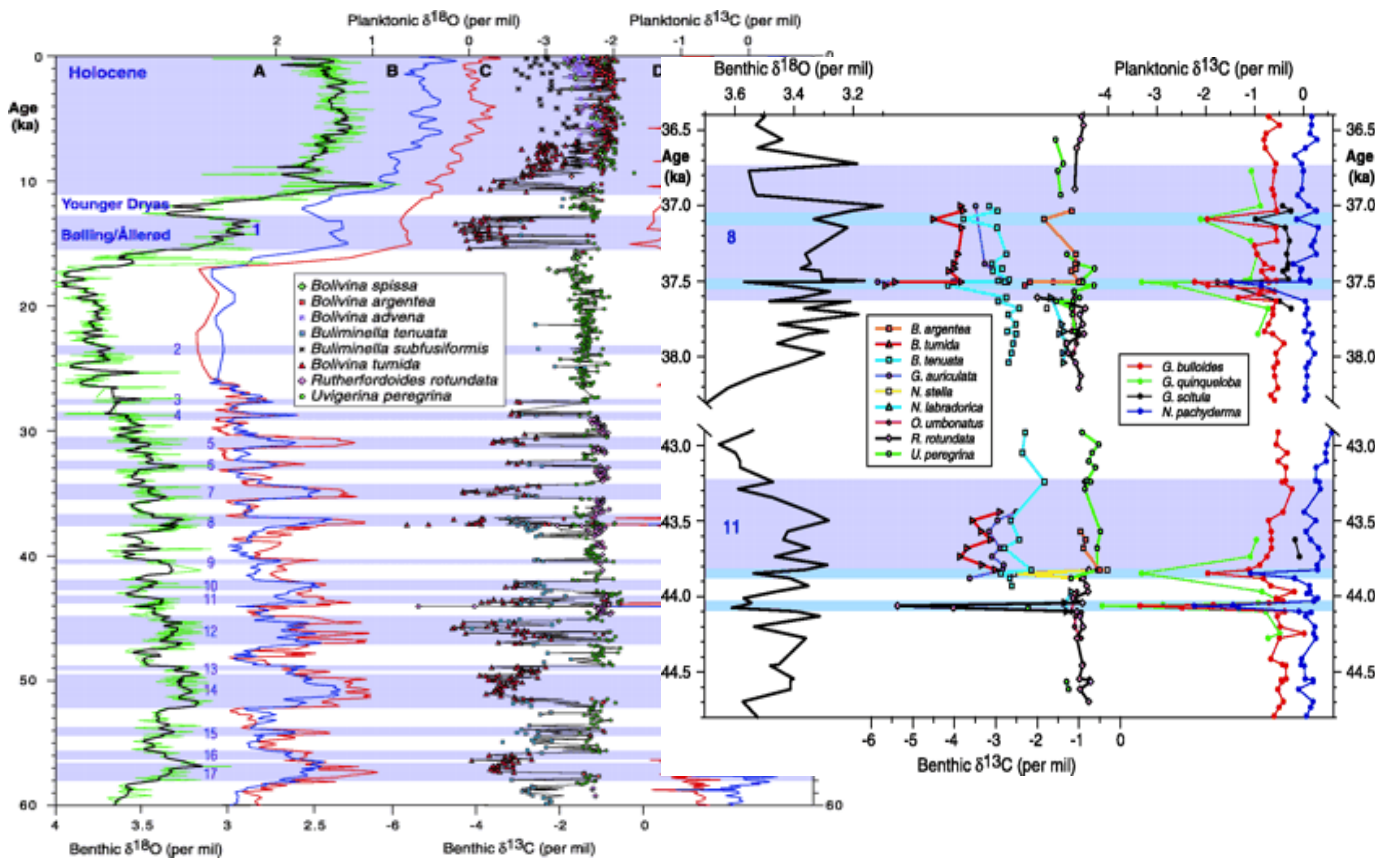
**Methane seeps environment:  $\delta^{13}\text{C}_{\text{DIC}} \cong -30 / -60\text{‰}$**

(Aharon *et al.*, 1992)

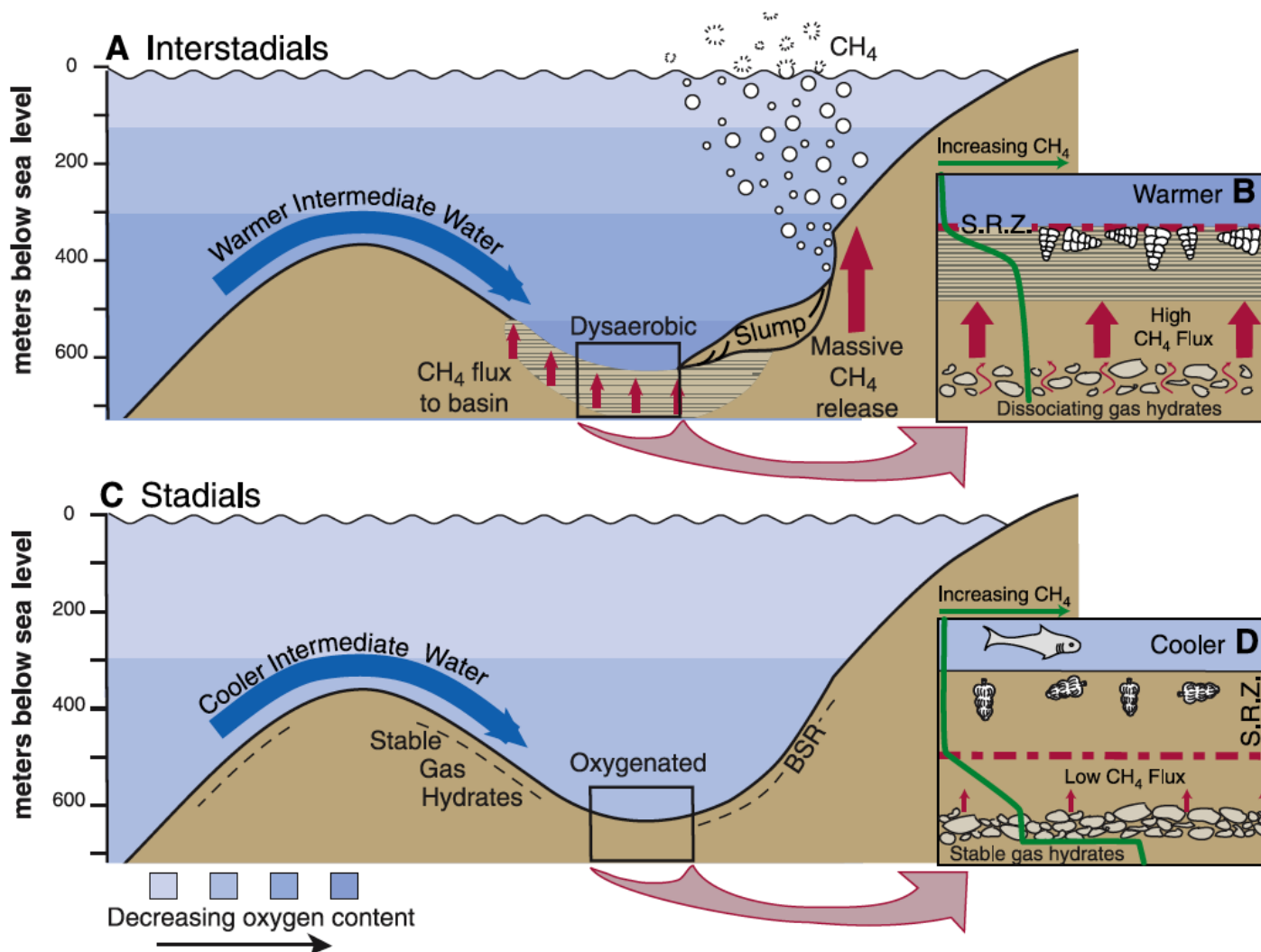




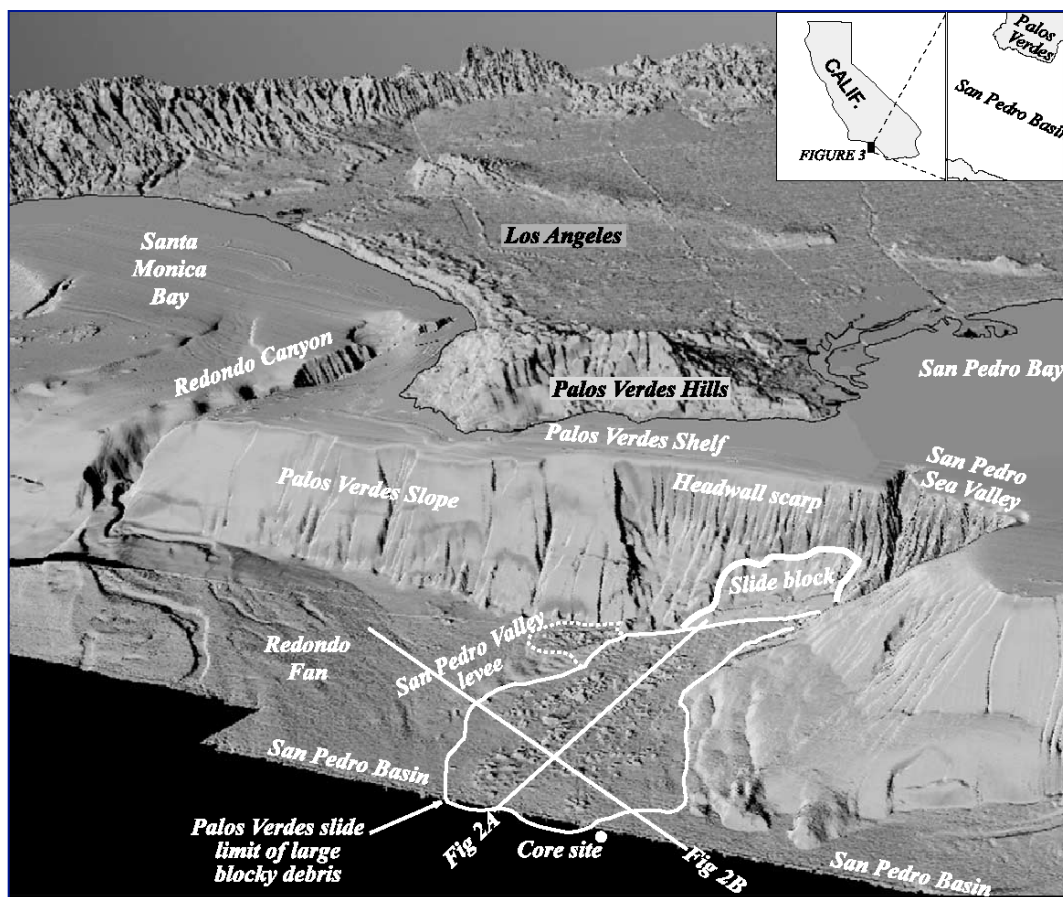
# Negative excursions of $\delta^{13}\text{C}$ in marine sediments during warm periods can be explained ONLY with massive emissions of Methane from the seafloor



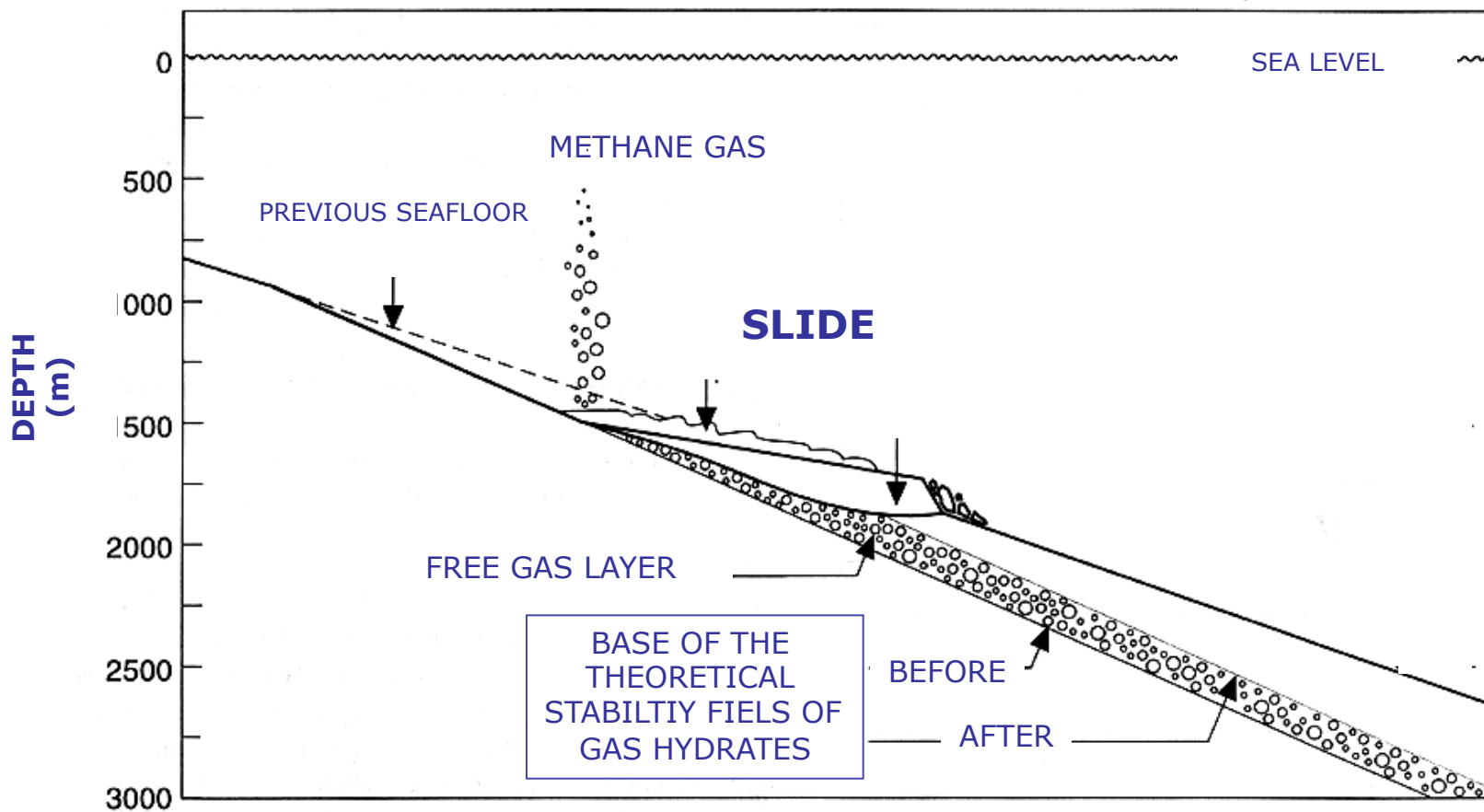
# The Clathrate Gun Hypothesis



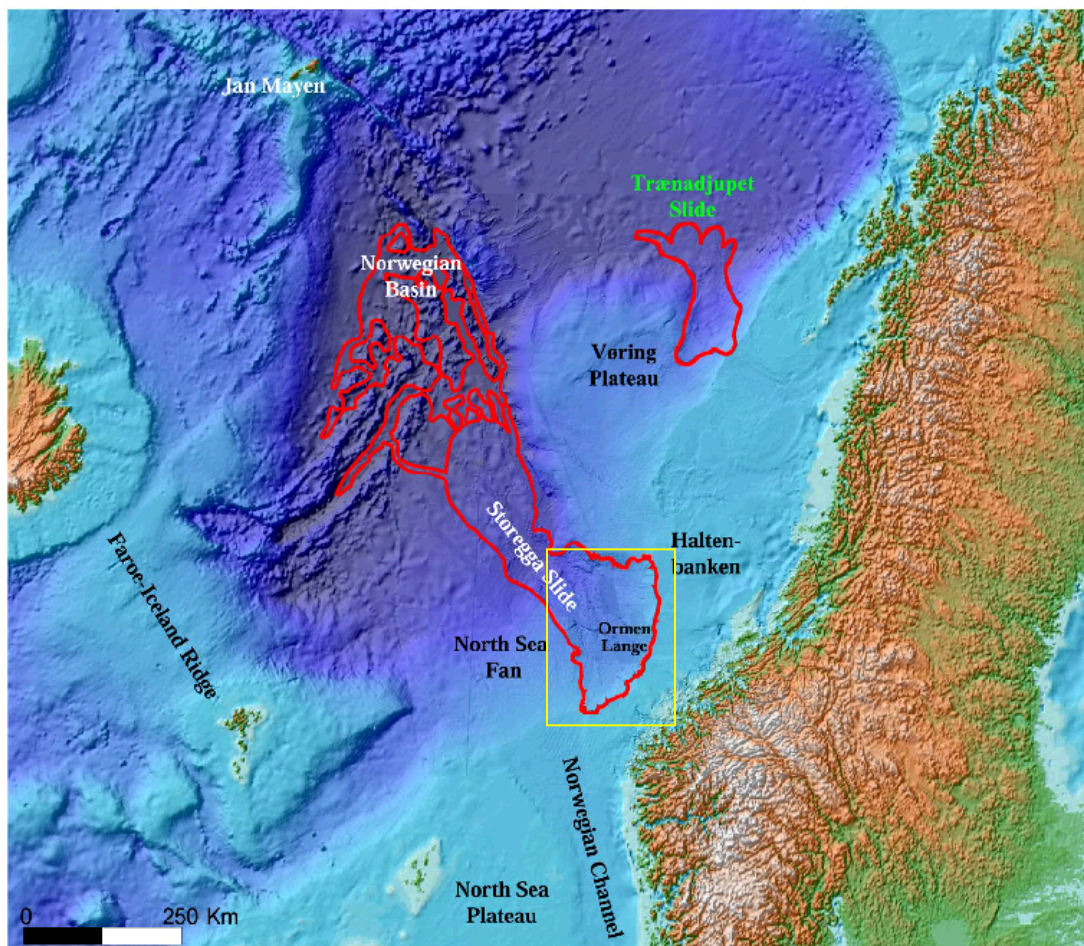
# Methane hydrate dissociation as source of submarine slope instability



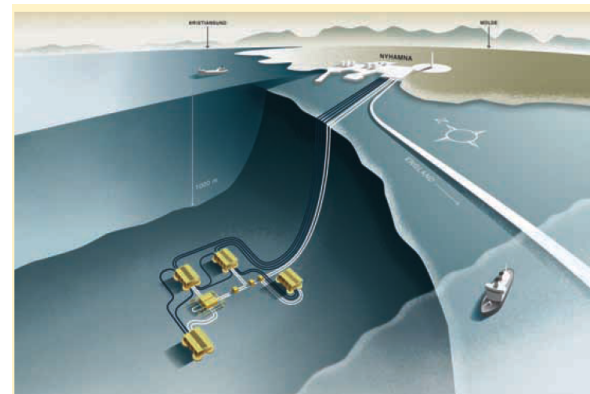
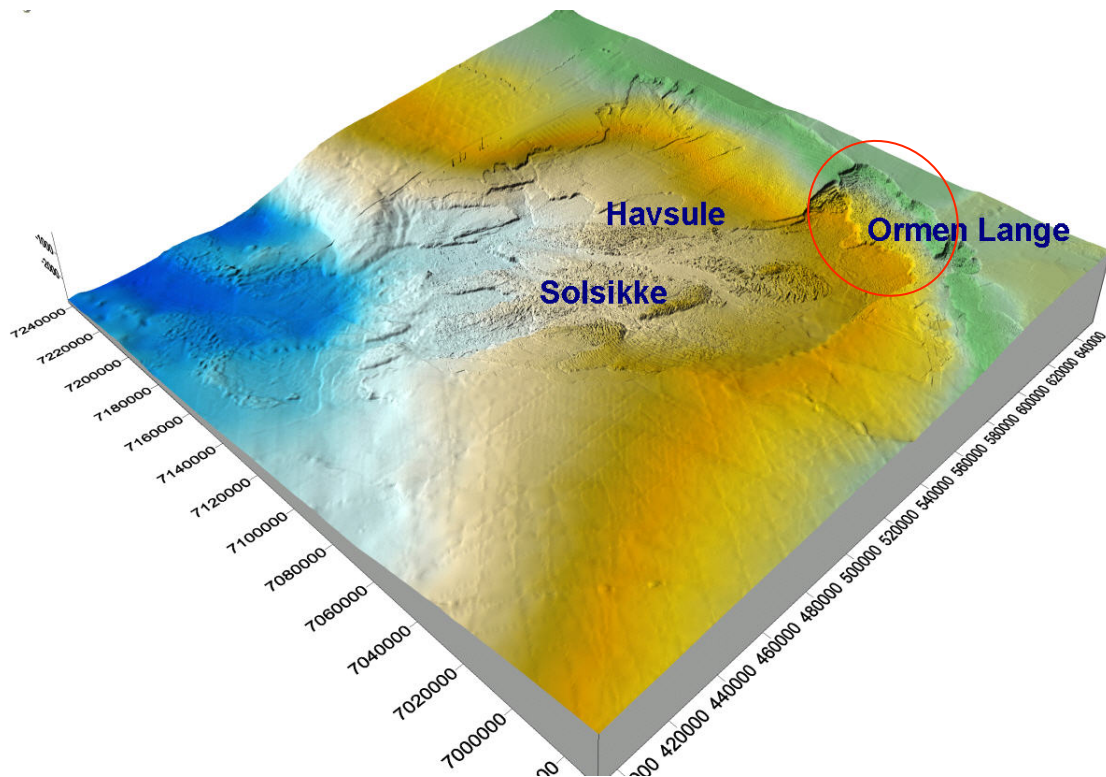
## GLOBAL WARMING



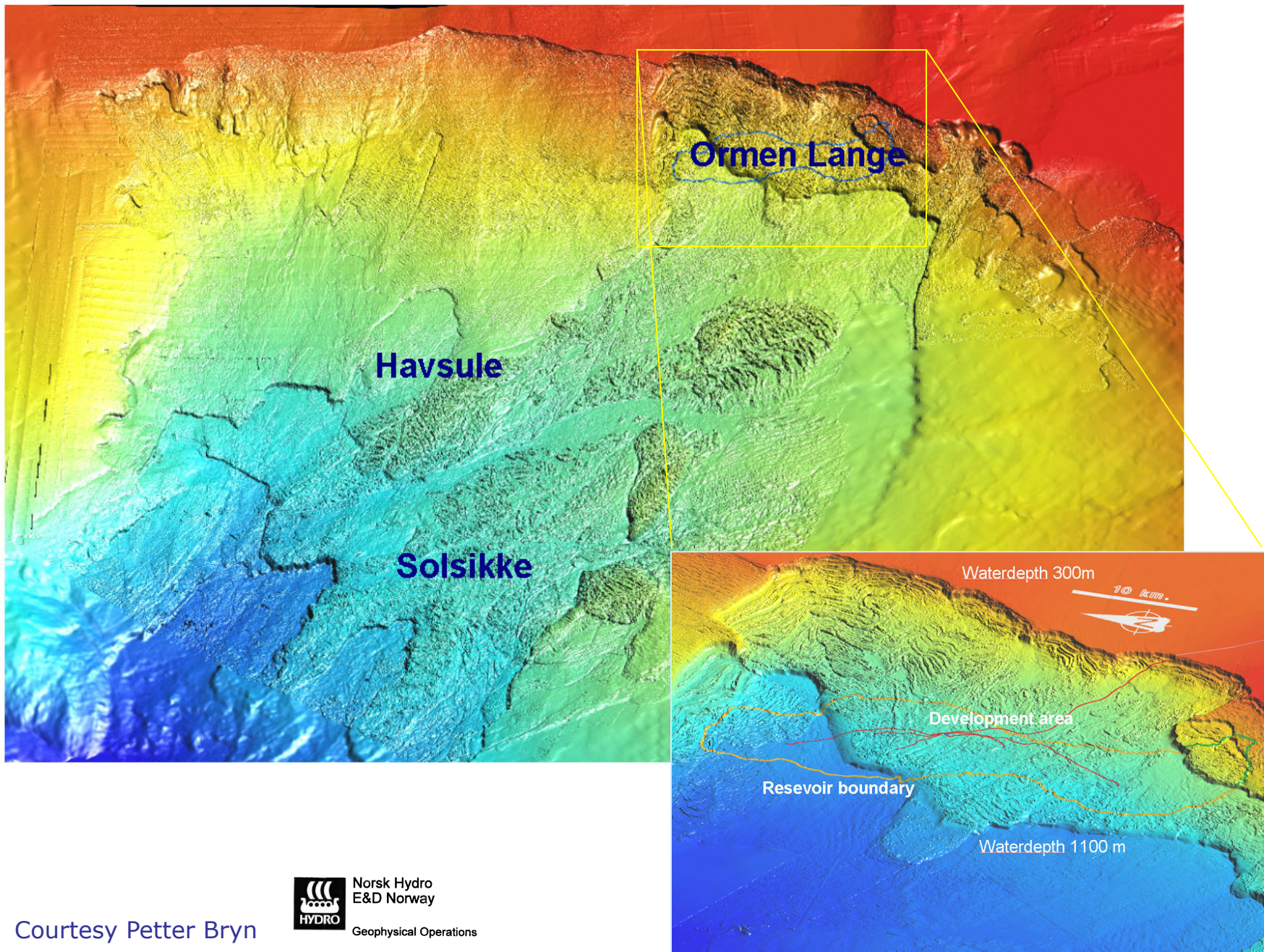
# THE STOREGGA SLIDE ON THE NORWEGIAN CONTINENTAL MARGIN (7000 yr)



Courtesy Petter Bryn



Courtesy Petter Bryn



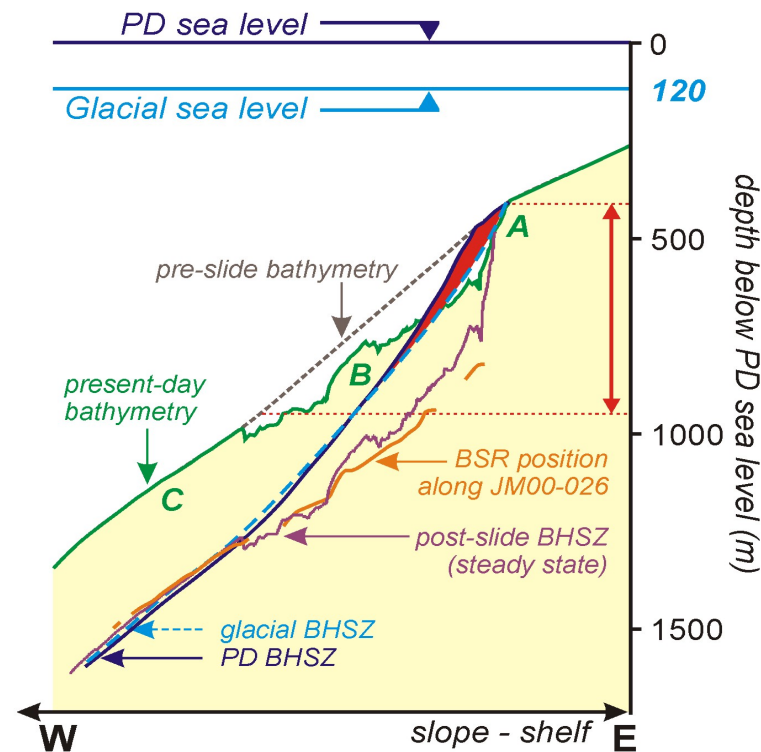
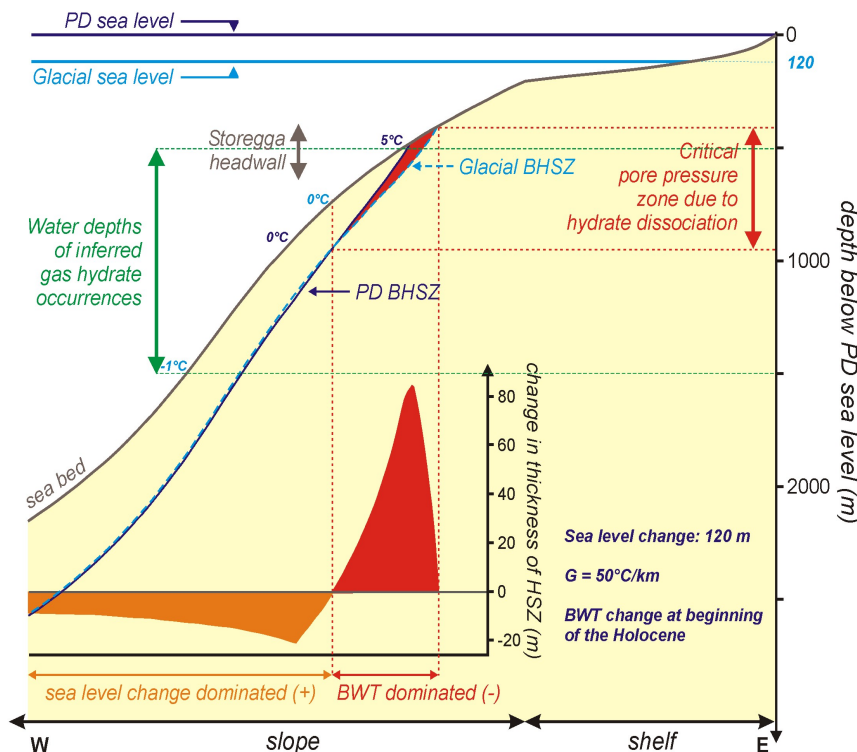
Courtesy Petter Bryn



## THE STOREGGA SLIDE CAUSED A HUGE TSUNAMI



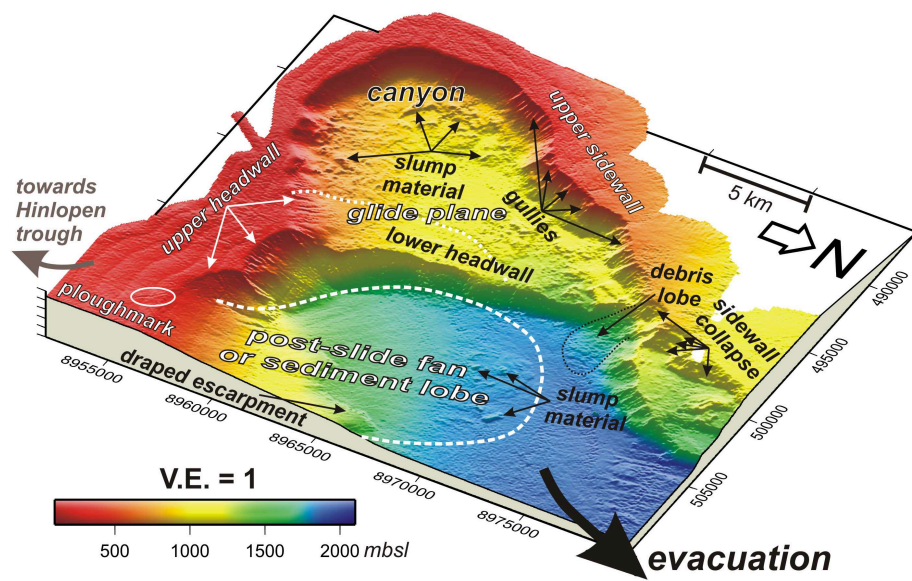
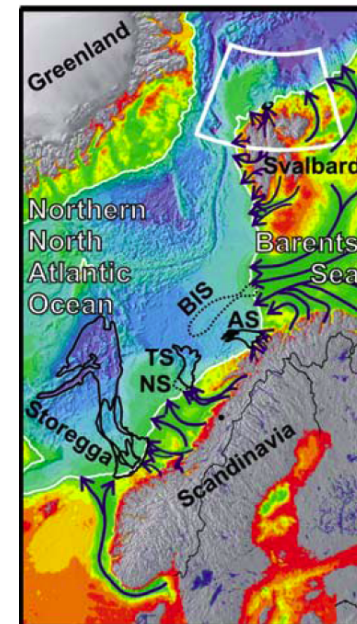
# The effect of gas hydrates



Mienert et al., 2005

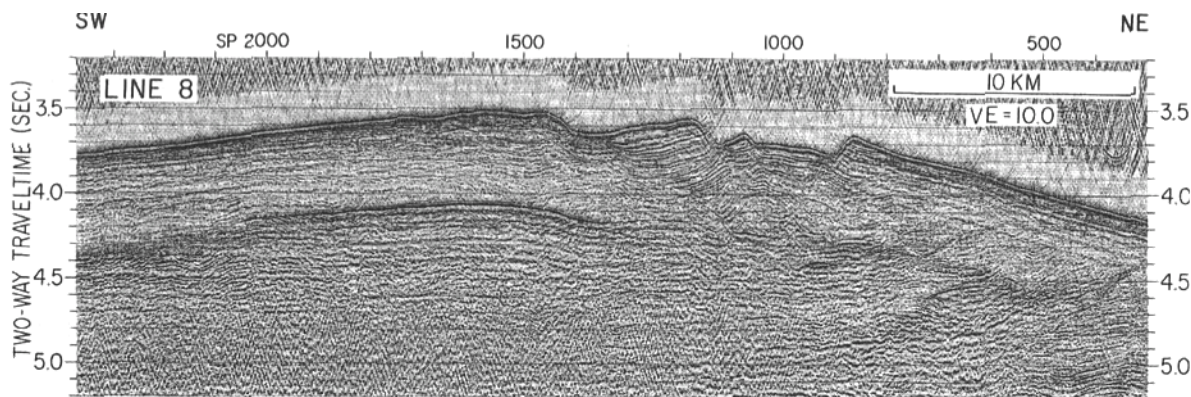
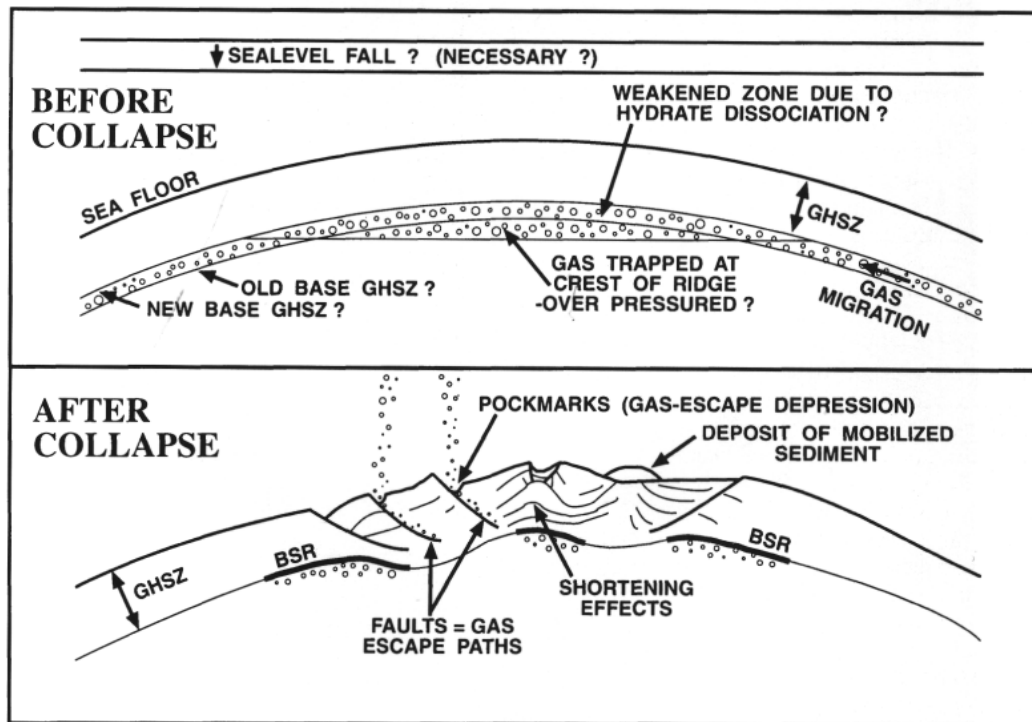
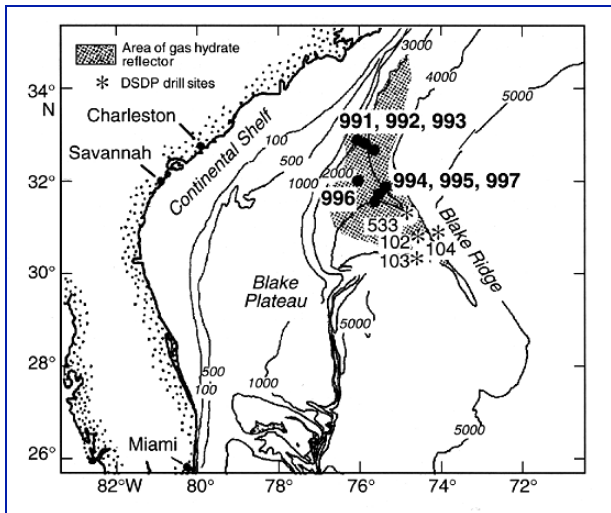
**Change in theoretical thickness of hydrate stability zone due to sea level change (small, negative) and bottom water temperature (locally large, positive). Biggest effect near upper headwall in Storegga.**

# THE NORTH SVALBARD SLIDE



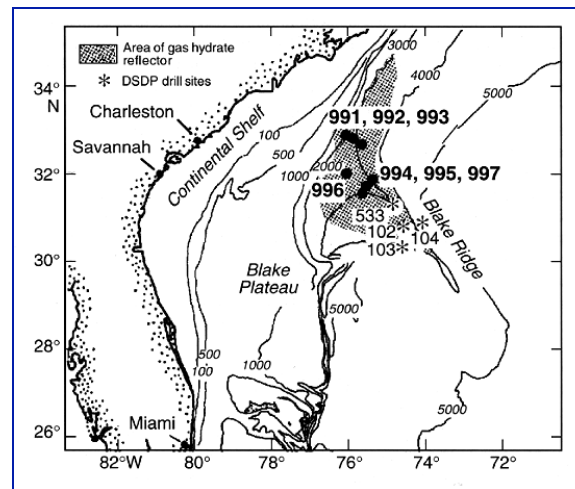
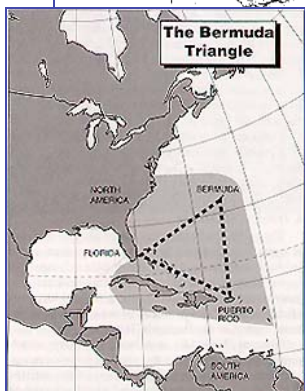
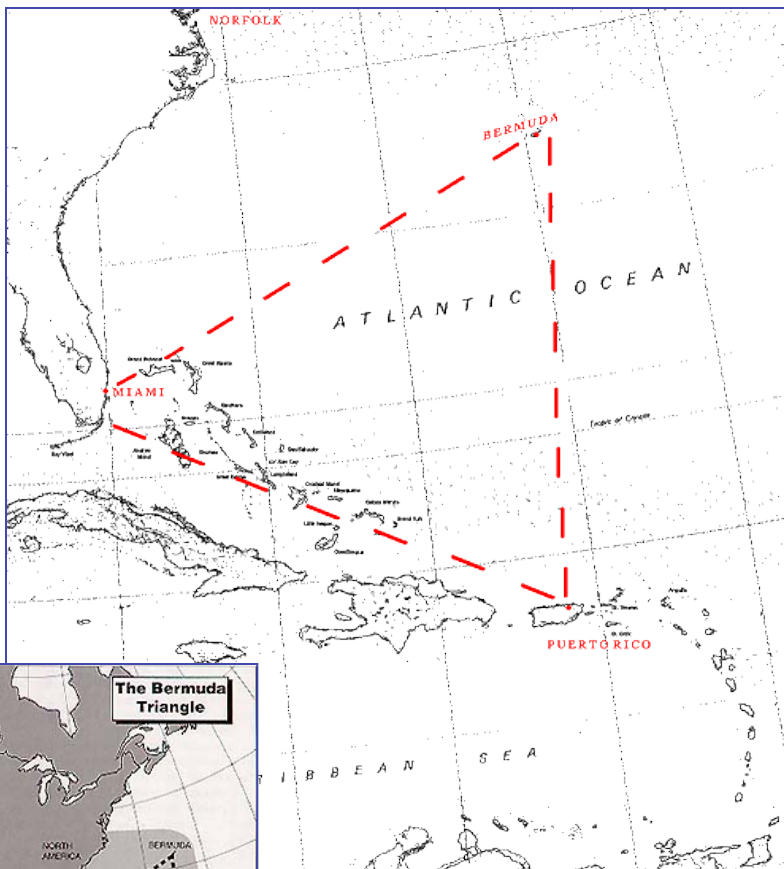
Vanneste et al., EPSL, 2006

# BLAKE RIDGE

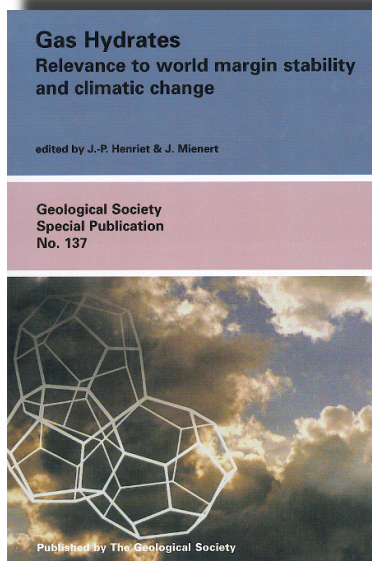


(Dillon et al., 1998)

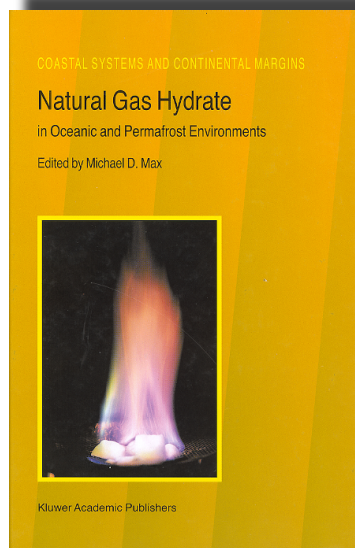
# AT THE EDGE OF SCIENCE



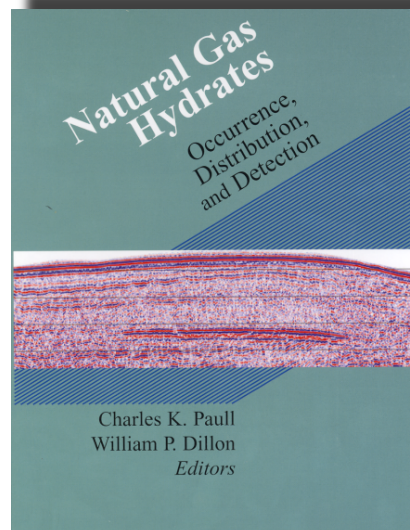
## 4 scientific books



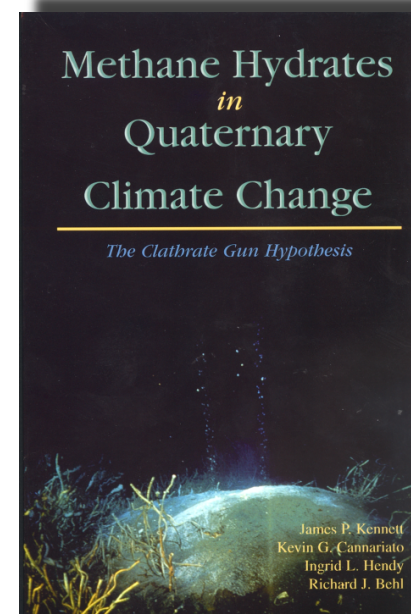
1998



2000



2001



2003



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