

# Physical and chemical processes affecting release of CO<sub>2</sub> at the seafloor

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*and thanks to colleagues: Ilker Fer, Joakim Hove, Peter Brewer et al.*



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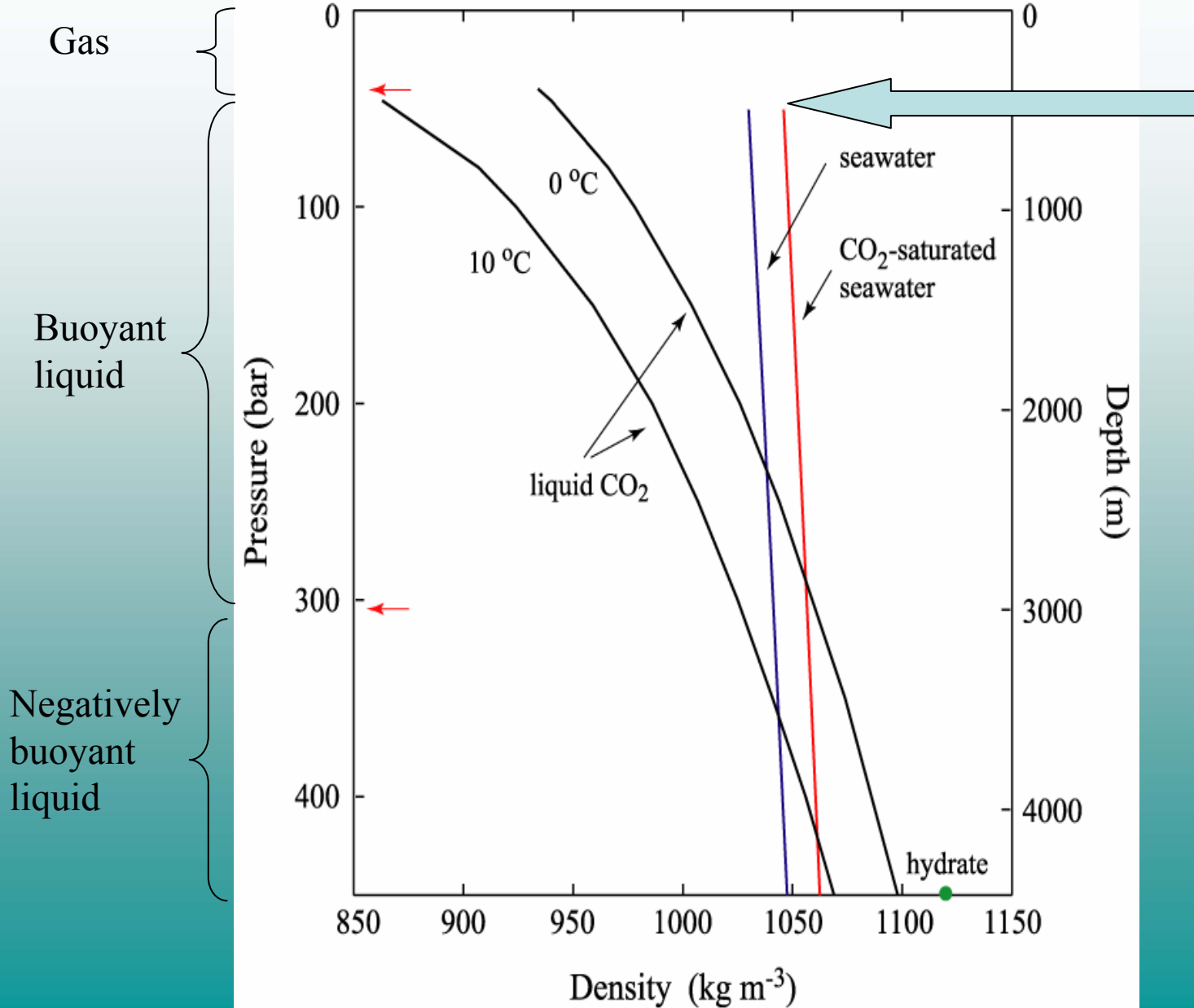
# Knowledge base relevant to CO<sub>2</sub> at the seafloor

- General theoretical, modelling and laboratory research on direct ocean storage of CO<sub>2</sub>
- 10-15 years ago, the "lake option" was proposed and studied theoretically based on lab properties.
- Lessons from observations of natural CO<sub>2</sub> vent systems, brine pools and gravity currents.
- Recent small scale experimental work with advanced ROV and observational techniques (Brewer et. al.).
- No *in situ* experiments on the bottom boundary layer (BBL) scale.
- Few published studies on deep sea BBL turbulence and hydrodynamics for an active tracer like CO<sub>2</sub>.

# Outline

- The ways in which CO<sub>2</sub> may be released at the seafloor
  - Gas bubbles
  - Liquid droplets
  - Liquid CO<sub>2</sub> "lake" or "pool"
  - Hydrate
  - Solid (dry ice)
  - Predissolved in water
- Dissolution from a deep sea pool of liquid CO<sub>2</sub>
- Mixing in the benthic boundary layer
- Gravity current dynamics
- Challenges and ongoing numerical modelling

# Density of seawater, liquid CO<sub>2</sub>, hydrate and CO<sub>2</sub>-enriched seawater



Dissolving CO<sub>2</sub> in seawater always increases density of seawater.

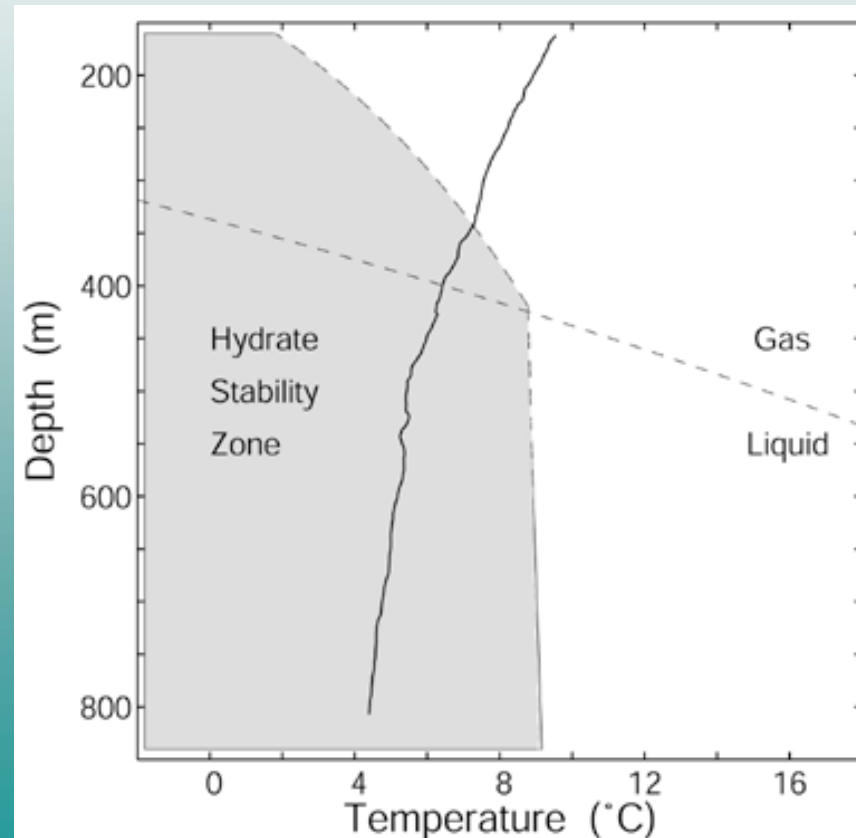
(Fer & Haugan, Limnol. & Oceanogr., 2003)

# Different ways of releasing CO<sub>2</sub>

- 1: Seepage at less than 400m depth makes CO<sub>2</sub> bubbles. However, CO<sub>2</sub> gas hydrates may form for water depths as shallow as 100m if water is sufficiently cold.

An interim hydrate stage with subsequent dissolution will contribute to keeping the CO<sub>2</sub> in place rather than escaping upwards in the gas phase.

One may speculate that a dense, CO<sub>2</sub>-enriched seawater layer could be created near the seafloor if seepage is slow.



## Different ways of releasing CO<sub>2</sub>

2: Slow seepage of small droplets into quiescent water in isolated depression or non-tidal basin may also create high concentration of dissolved CO<sub>2</sub>.

3: Seepage of pore water with predissolved CO<sub>2</sub>.

*All of 1-3 may be relevant to geological subseabed storage. Impact research for direct ocean storage could also be appropriate for seepage from geological storage (Haugan, Waste Mgmt., 1997).*

4: Direct deep ocean storage of seawater with predissolved CO<sub>2</sub> (e.g. Saito et al. (2000) Gas Lift Advanced Dissolution concept).

## Different ways of releasing CO<sub>2</sub>

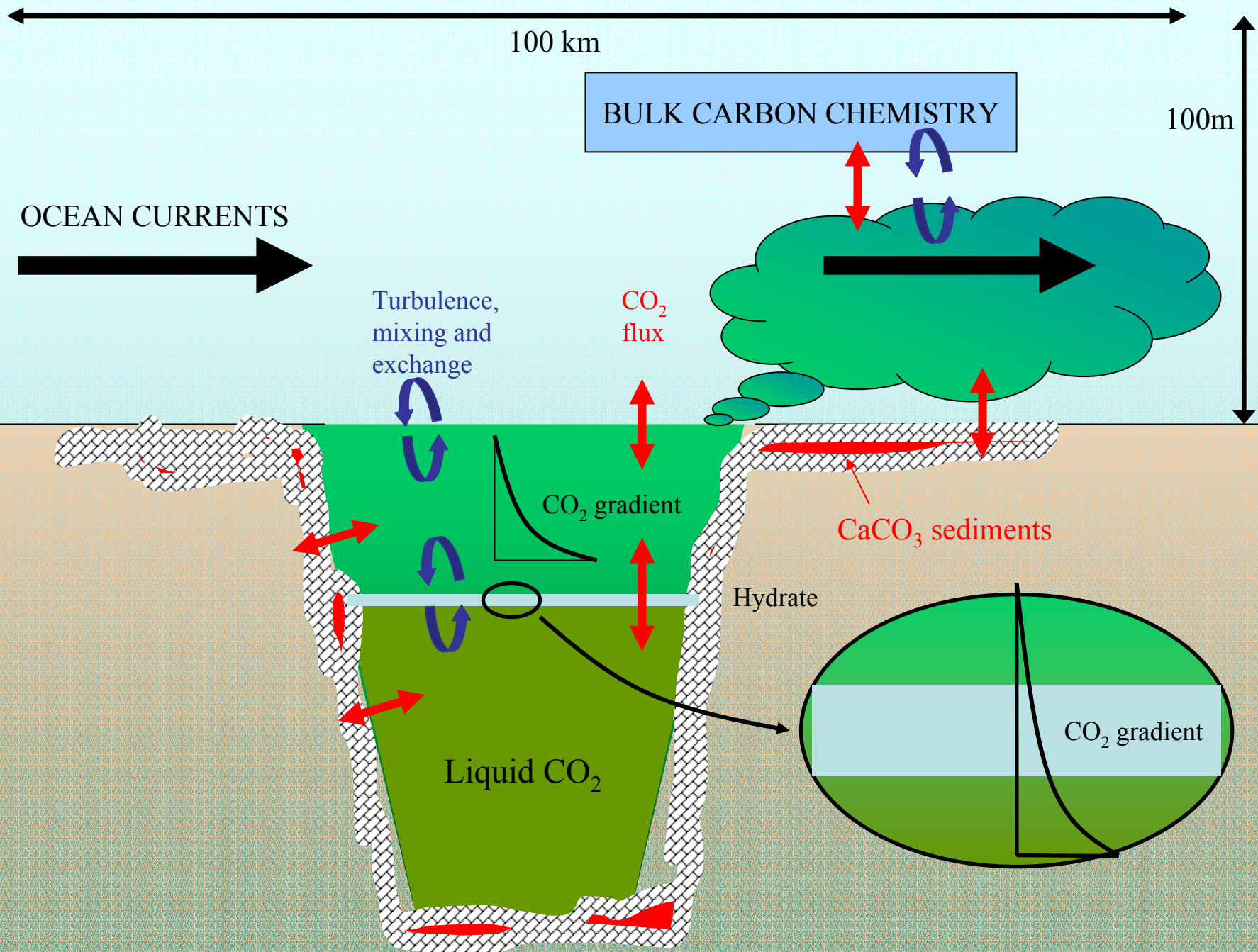
All of 1 - 4 will create a layer of dense, low pH water spreading along the seafloor as a gravity current unless obstructed by topography.

5: Release at less than 400m in warm water implies rapid escape to the atmosphere.

6: Release of dry ice is impractical and costly.

7: Release of buoyant droplets and dynamics of droplet plumes are covered in talk by Chen.

8: Main focus hereafter on deep sea pool dissolution, vertical mixing, gravity current.





# Release from a pool of CO<sub>2</sub>

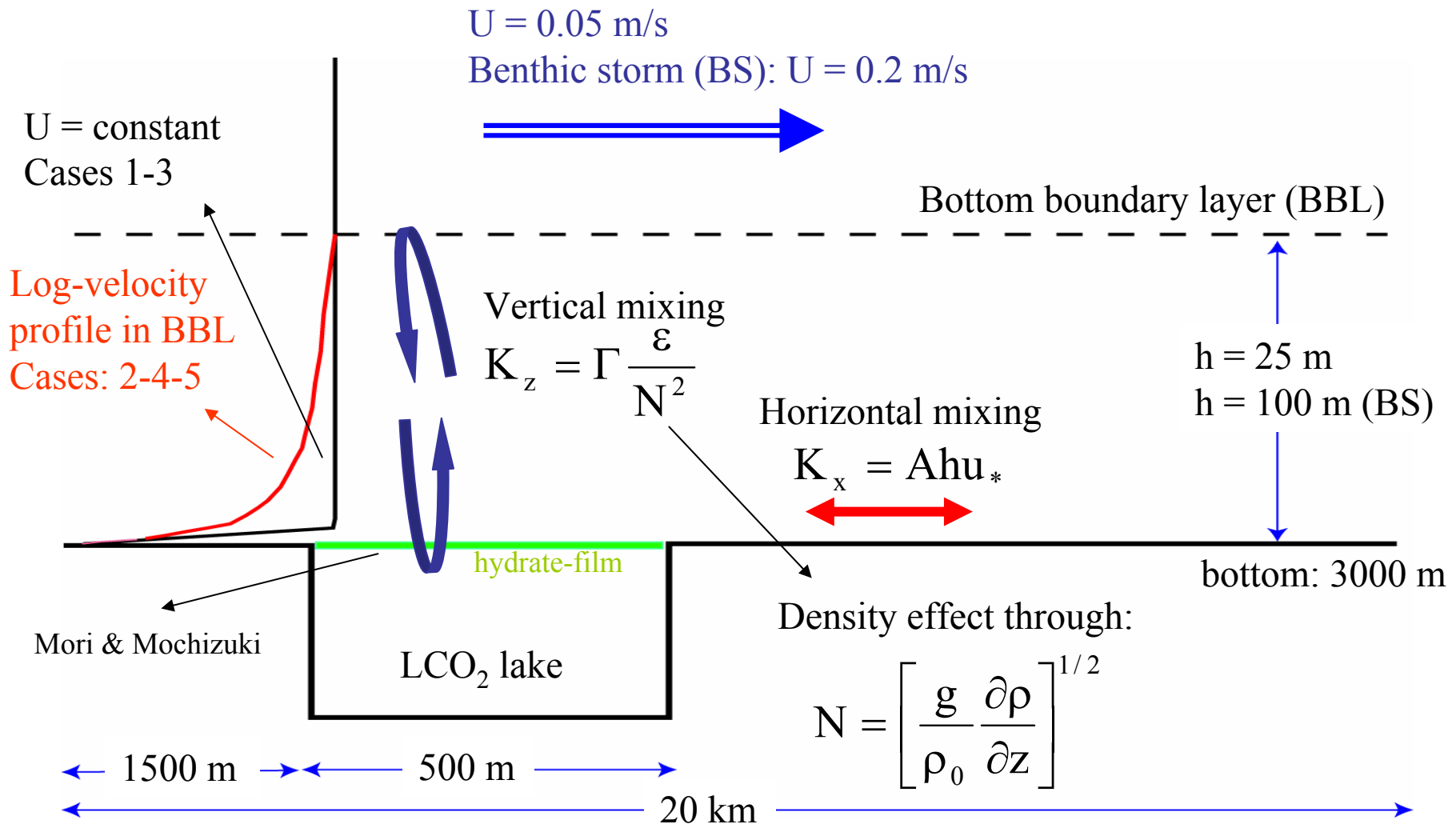
- One experiment with CO<sub>2</sub> exposed to natural currents at 684m depth (Brewer et al., J.O., 2004, in press)
- One experiment with controlled dynamic perturbation (thruster and wavemaker) ~ 50 liter, 3940m:



# Preliminary results from controlled experiment

- Interfacial wave dispersion relation from analysis of video imagery for various wavemaker wavelengths
  - Interfacial deep "water" gravity waves
- Stability – instability transition from sequence of thruster experiments
  - Critical velocity identified ( $\sim 18$  cm/s at 3940m depth)
- Energy content by wavelet analysis of interface
  - Peak energy at about 1cm, close to theoretical wavelength of maximum growth rate for Kelvin-Helmholtz instability between CO<sub>2</sub> and water (depending on interfacial tension)

# A model with dissolution-turbulence coupling



Unsteady, 2D advection-diffusion equation:

$$\frac{\partial C}{\partial t} + \frac{\partial (uC)}{\partial x} + \frac{\partial (wC)}{\partial z} = \frac{\partial}{\partial x} \left( K_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial C}{\partial z} \right)$$

Domain: 20 km x 200 m at flat ocean bottom at 3000 m depth.

Source: A liquid CO<sub>2</sub> lake of 500 m span at 1500-2000 m from origin.

Grid resolution: 250 m in horizontal, 1.25 - 5 m in vertical.

Simple BBL theory:

$$\varepsilon(z) = \frac{\tau_0}{\rho} \frac{\partial U}{\partial z} = \frac{u_*^3}{\kappa z}$$

where  $\varepsilon$  is turbulent kinetic energy dissipation rate,

$\tau_0$  is shear stress at the bottom,

$u_*$  is friction velocity, and

$\kappa$  is von Karmans constant.

Mass transfer proportional to  $u^*$

# Capillary permeation model (Mori & Mochizuki, 1997)

Molar flux of liquid CO<sub>2</sub> into the water phase:

$$J_{\text{CO}_2} = \frac{1}{1 - \tilde{C}_s} \left[ K_m \frac{\rho_{\text{mix}}}{M_{\text{mix}}} (\tilde{C}_s - \tilde{C}_{\text{amb}}) - \frac{\tilde{C}_s}{1 - \tilde{C}_s} J_w \right]$$

Molar flux of water through the hydrate:

$$J_w = f(\delta, M_{\text{mix}}, v_{\text{mix}})$$

Hydrate thickness:

$$\delta = f(\gamma, \phi, r_c, p, \tau, \eta_{\text{mix}}, C_s, n, K_m)$$

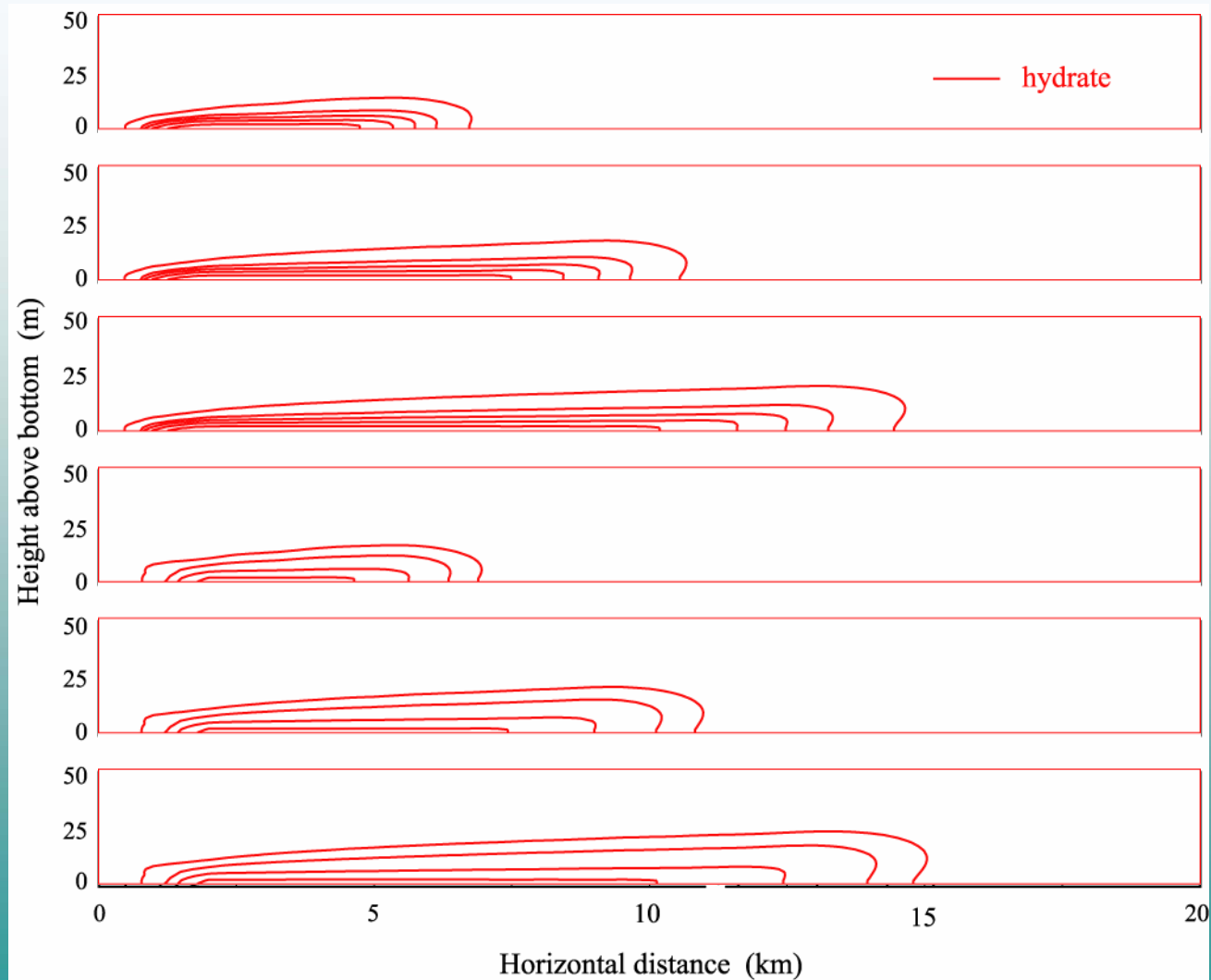
Tortuosity,  $\tau = 2$ ; Porosity,  $p = 10^{-3}$ , Capillary radius,  $r_c = 10^{-8}$  m

Interfacial tension,  $\sigma = 19.4 \times 10^{-3}$  N m<sup>-1</sup>, Contact angle,  $\phi = 0^\circ$

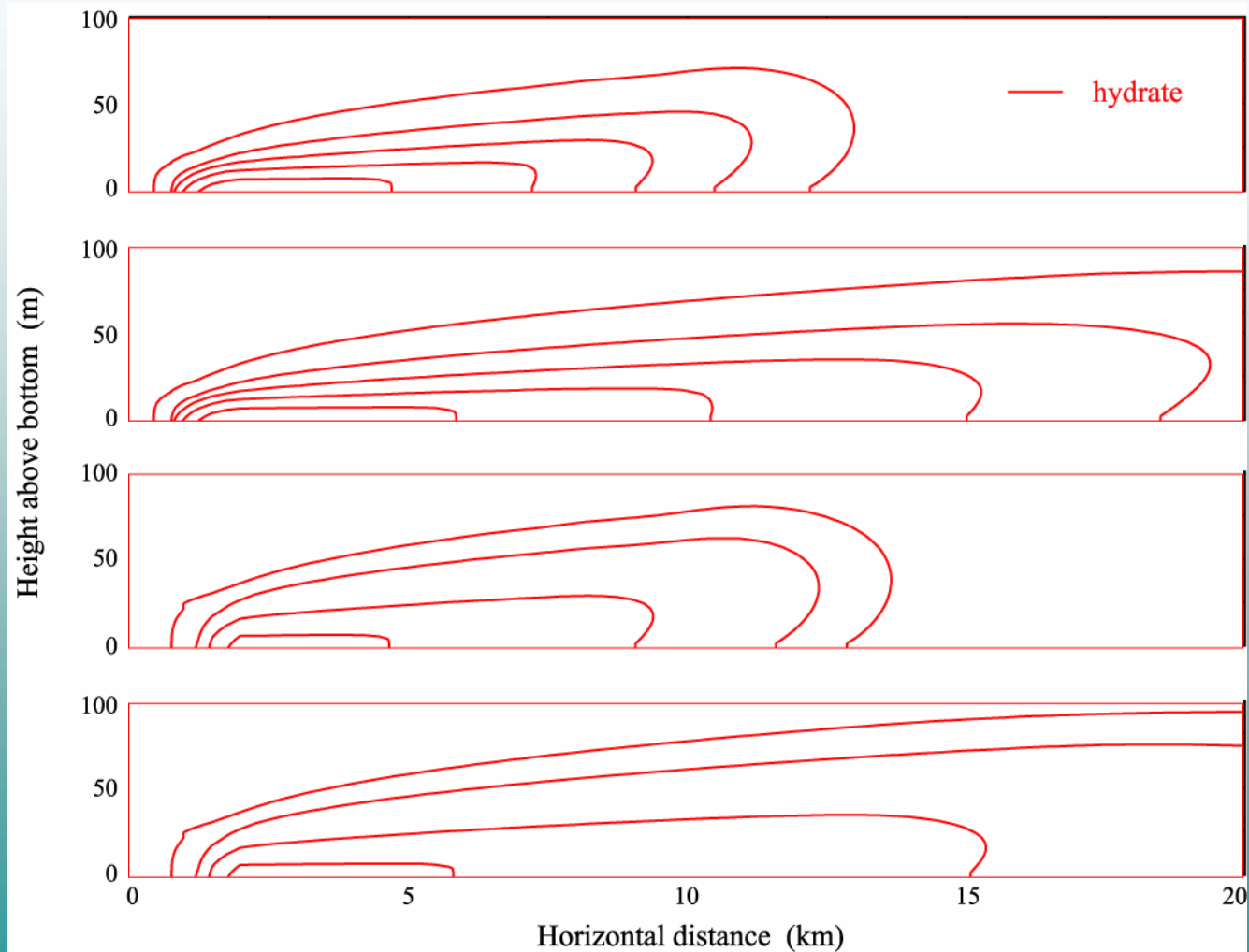
Hydration number,  $n = 5.75$

Mass transfer coefficient:  $K_m = 0.1 u_* \text{Sc}^{-0.67}$

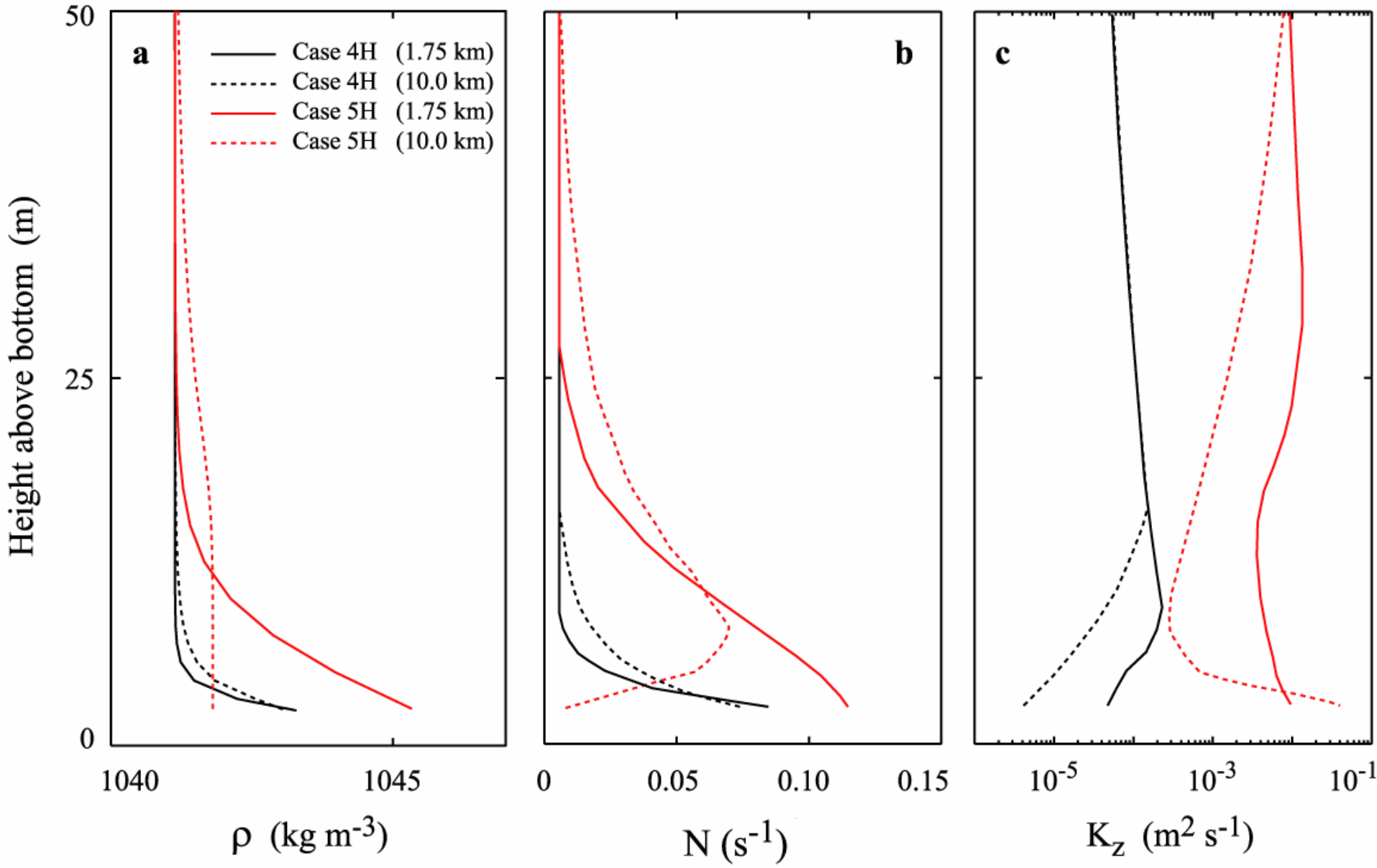
# Standard case with BBL profiles (case 4 and 4H)



# Benthic storm (case 5 and 5H)

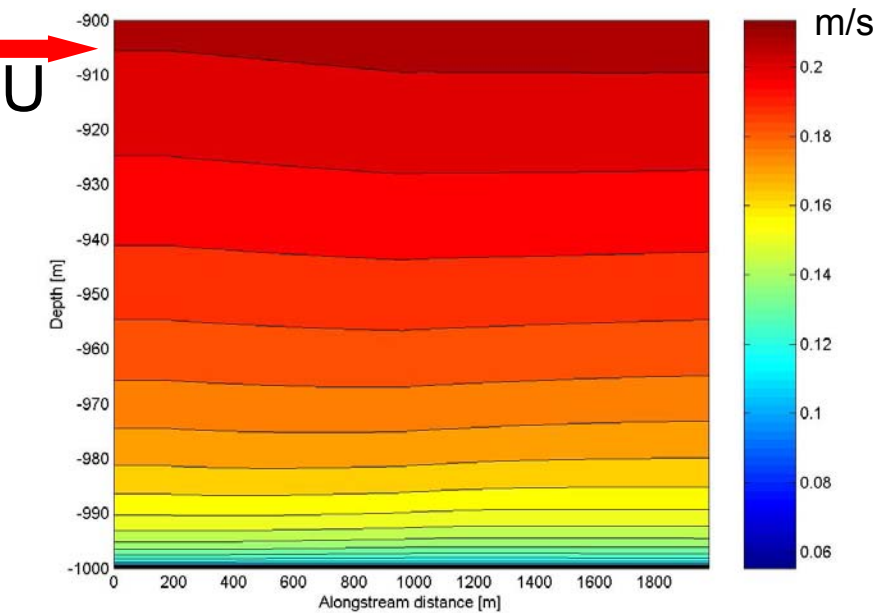


# Density, buoyancy frequency and vertical diffusivity profiles





## Lower 100m

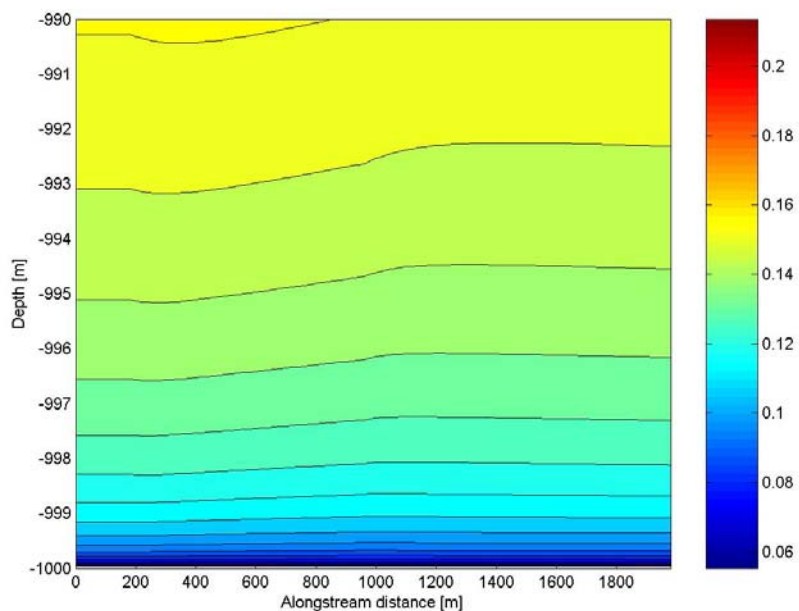


## New model study in progress

### Near equilibrium velocity (after 20 hours)

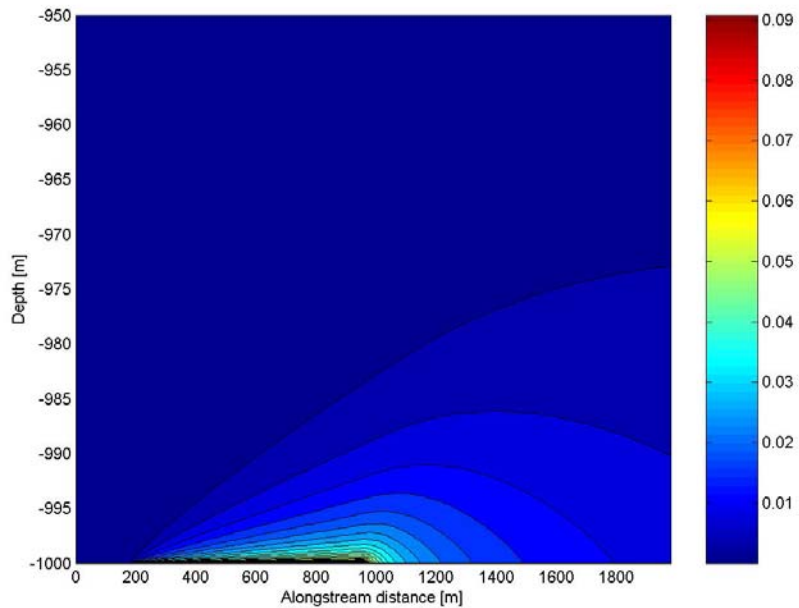
- 2000m by 1000m domain
- Specified  $\text{CO}_2$  flux at seafloor between  $x=200\text{m}$  and  $x=1000\text{m}$
- $dx = 20\text{m}$
- $dz$  varying from 7cm to several m in 400 points over 1000m.
- $k-\varepsilon$  turbulence model
- 20 cm/s background current from left to right in this case

## Lower 10m



←  $\text{CO}_2$  source →

## Lower 50m

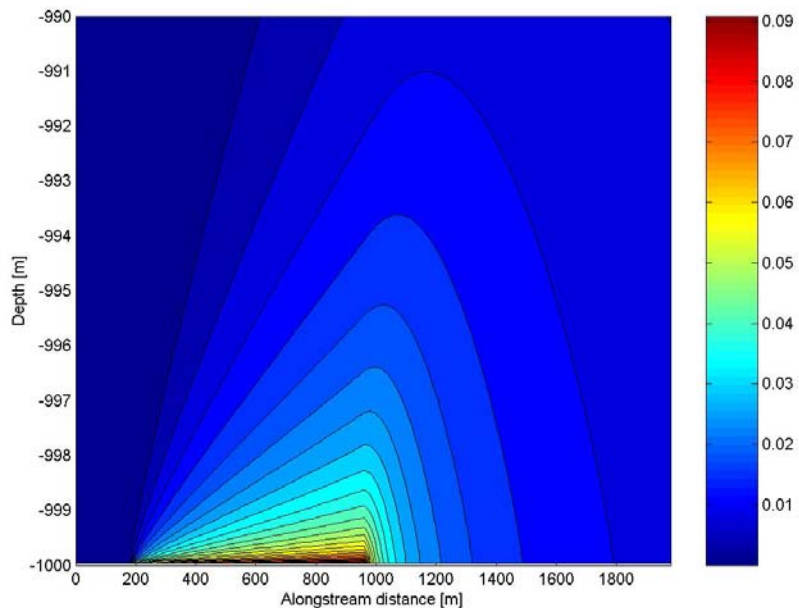


## Carbon concentration (20 hours, 20 cm/s current)

Unpublished work addressing:

- Concentrations, pH values, horizontal and vertical scales
- Turbulence closure models
- Effects of ambient stratification
- Importance of density effect for different conditions
- Characterization of outflowing plume which may progress by stable gravity current dynamics

## Lower 10m



CO<sub>2</sub> source

# Conclusions on dissolution and mixing

- Dissolution and vertical mixing processes are coupled.
- In models, CO<sub>2</sub>-induced stable stratification above the hydrate layer suppresses mixing considerably. This reduces the importance of hydrate to retard dissolution.
- Modelled dissolution from less than 1 cm y<sup>-1</sup> in purely diffusive regime with no velocity (Ohsumi, 1997) to about 10 cm y<sup>-1</sup> in low velocity regime and more than 1 m y<sup>-1</sup> in benthic storms (Fer & Haugan, 2003).
- Kelvin-Helmholtz instability has recently been experimentally confirmed in deep sea CO<sub>2</sub> experiment, but no build-up of dissolved CO<sub>2</sub> concentration.

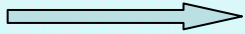
# Conclusions on dissolution and mixing

- Topography may shield against strong currents and reduce dissolution (Kobayashi, 2003).
- On the other hand, recirculation could lead to build up of high concentration, and overspill associated with internal seiching could occur in sill basin.
- Long term large rate experiment would be required to check concentration profile in water above CO<sub>2</sub> pool.
- Brine pools are natural analogues, but often have larger density contrast.
- Outflowing plume from pool area is expected to form gravity current.

# DEVELOPMENT OF GRAVITY CURRENT

100m

BACKGROUND CURRENT



Turbulence,  
mixing and  
exchange



CO<sub>2</sub>  
flux



BACKGROUND + GRAVITY CURRENT



CO<sub>2</sub> gradient

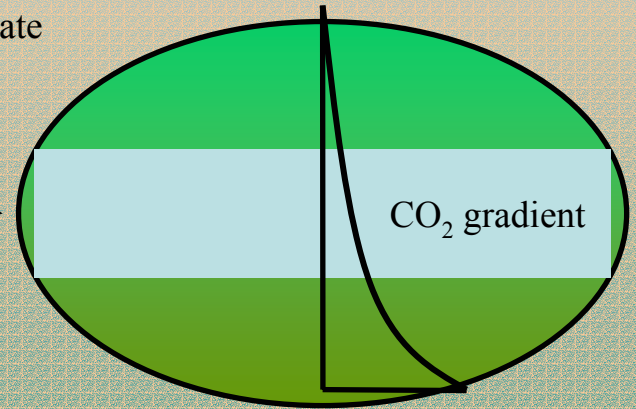


CaCO<sub>3</sub> sediments

Hydrate

Liquid CO<sub>2</sub>

CO<sub>2</sub> gradient



# Gravity current dynamics

- A slope of only about  $4 \times 10^{-3}$  (2 times the drag coefficient) may lead to a steady gravity current.
- Classical gravity current models are formulated for homogeneous layers. A rich literature is based on laboratory studies.
- Gravity currents with  $\text{CO}_2$ -enriched water have been modelled and studied as a vertical transport mechanism for  $\text{CO}_2$  (Drange & Haugan, 1993, Adams et al., 1995, Alendal, 1996).
- Gravity currents entrain ambient water. Mixing and entrainment is particularly strong near the transient head.
- Natural gravity currents in the ocean occur where dense water, typically at high latitudes, descend to ventilate deep water.
- Recent *in situ* observations have begun to explore internal structure previously only studied in models.

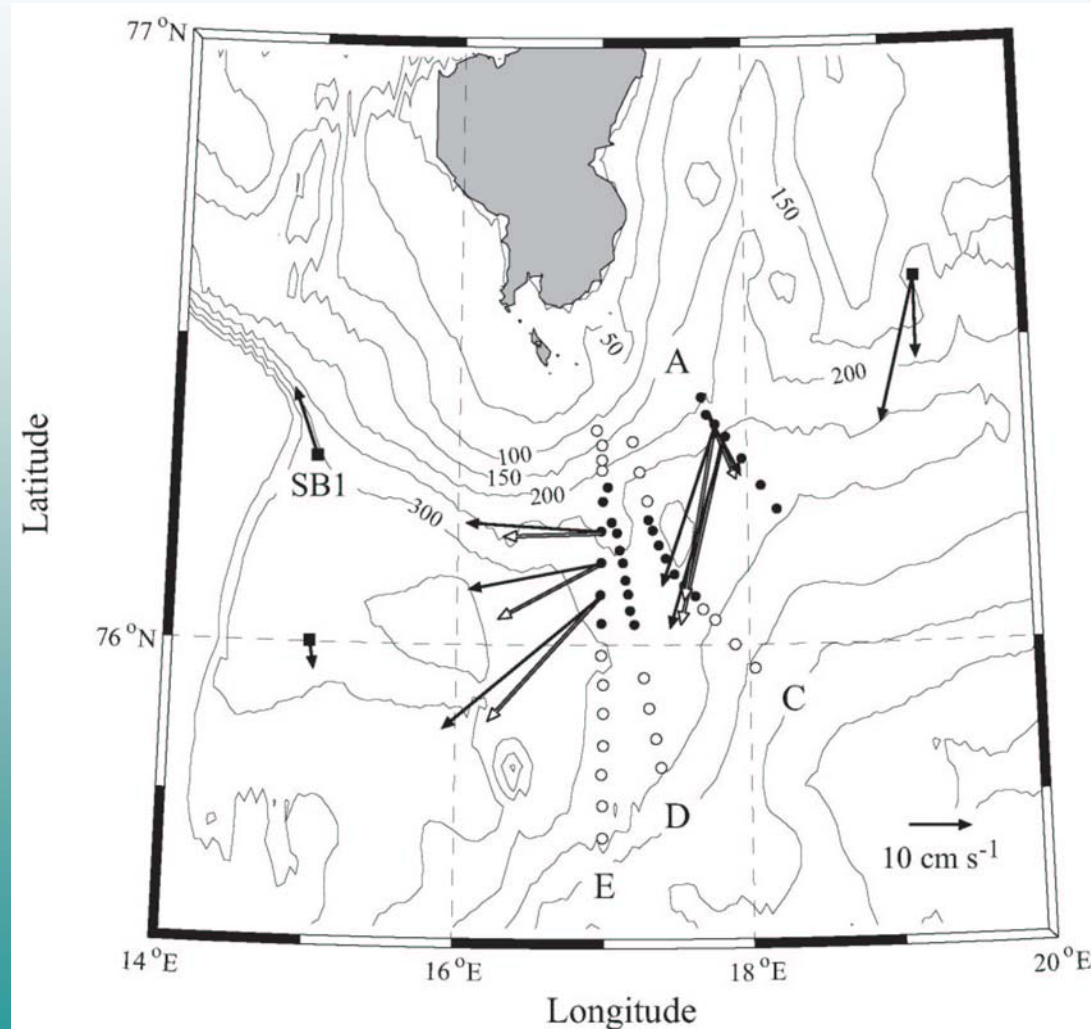


# Natural analogue gravity current: Observed outflow from basin with cooling and freezing/brine rejection

Storfjorden, Svalbard -  
Identified as two layers:

- 1) a lower layer (~15 m) with relatively uniform vertical structure
- 2) an upper, thick mixing layer (~30 m) with larger vertical density gradient

The widening of the lower layer is comparable to Ekman veering (friction from the bottom)



# Cross-section outflow

Vertical diffusivity (bars)

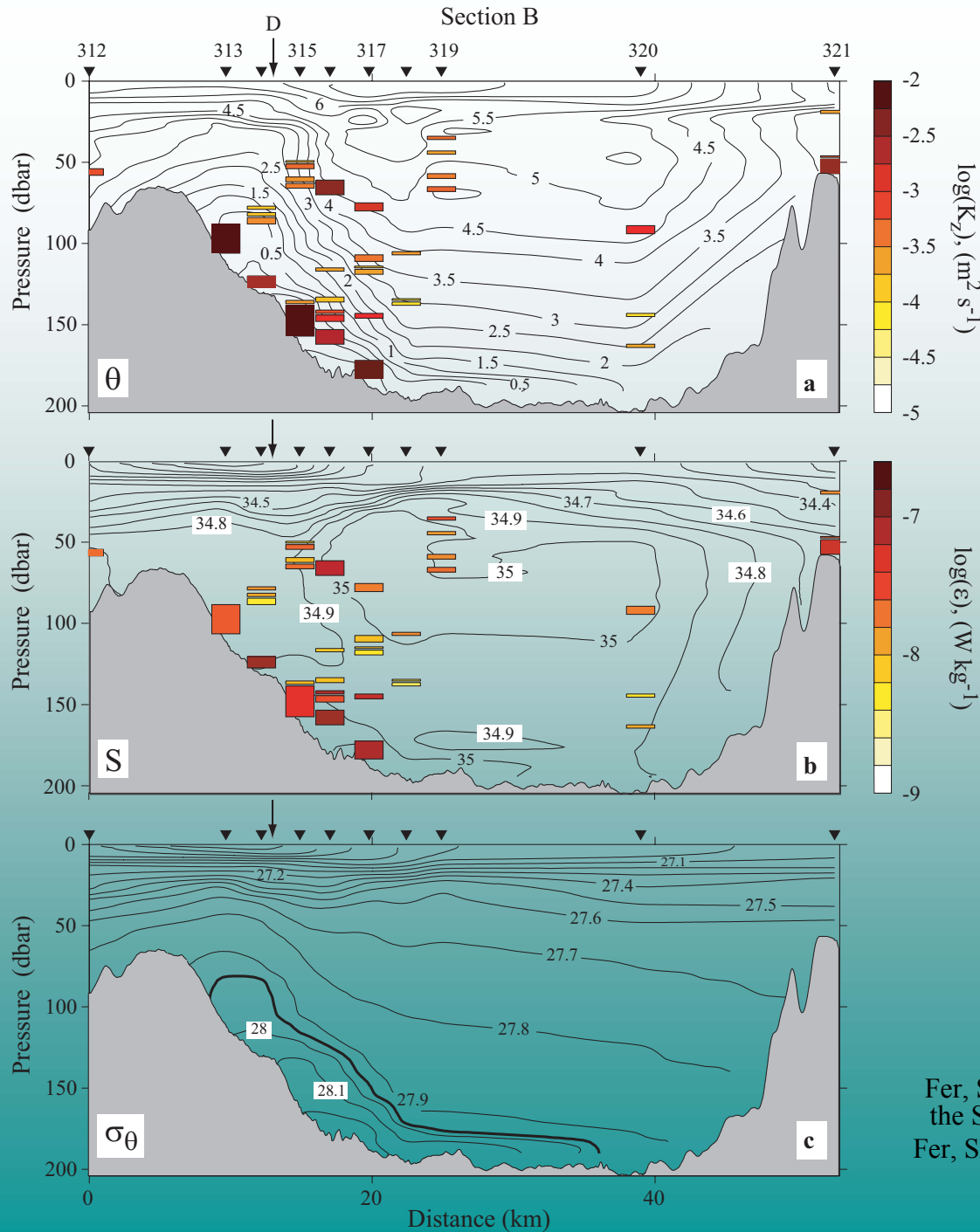
Temperature (contoured)

TKE dissipation (bars)

Salinity (contoured)

Potential density

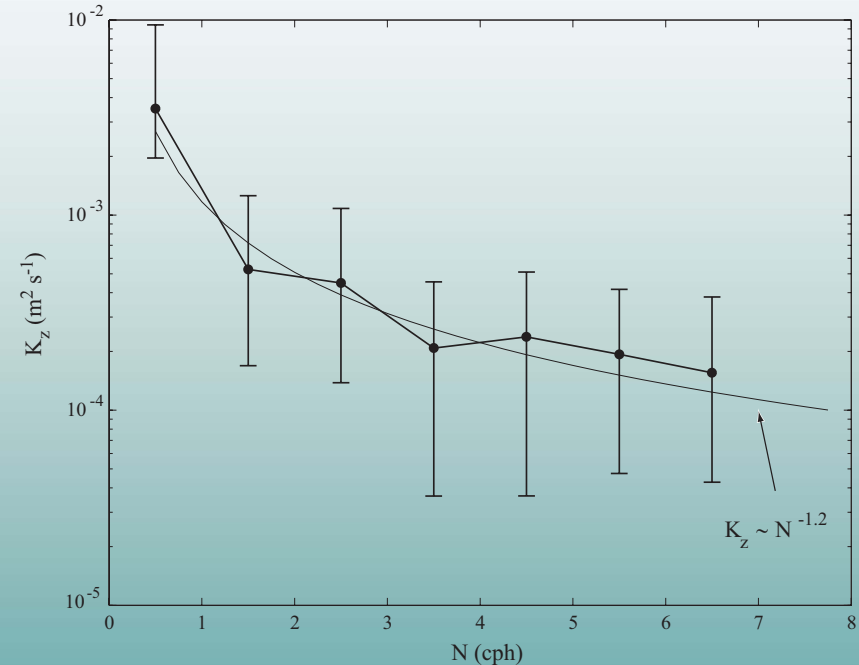
Fer, Skogseth, Haugan and Jaccard: Observations of the Storfjorden overflow, *Deep-Sea Research* 2003.  
Fer, Skogseth and Haugan: Mixing of the Storfjorden overflow (Svalbard Archipelago) inferred from density overturns, *J. geoph. res.* 2004.





# Dynamics of a dense outflow

- Lower part of dense plume is homogenized by turbulence from bottom irregularities.
- Upper part of dense plume mixes with ambient water due to shear induced mixing (vertical diffusivity is decreasing with increasing buoyancy frequency as  $N^{-1.2}$  ).
- This may be relevant to deep sea  $\text{CO}_2$ -enriched seawater plume depending on slope and carbon concentration.



# Turbulence Profiling

- microstructure, turbulence, and standard CTD Sensors
- allows direct estimate of mixing and elucidation of mixing process
- presently free fall from surface
- could be run free rising from seafloor in the deep sea



MSS



# Conclusions and challenges

Many technical options for direct storage would ultimately deliver the CO<sub>2</sub> in dissolved form in a dense, low pH, near bottom layer.

The carbon concentration in such a layer and its mixing and spreading would be crucial to sediment interaction, benthic life, dilution in the pelagic domain, and efficiency.

Preliminary model studies based on very limited *in situ* data give dissolution estimates for deep sea liquid CO<sub>2</sub> pools depending on the current regime.

Models furthermore suggest the development of a dense internal boundary layer within the BBL.

# Challenges

What is the lifetime and space scale of elevated carbon concentrations? When does the BBL homogenize at sufficiently low carbon concentrations that further diffusion is reduced to a passive tracer problem?

Obtain general understanding of mixing between the BBL and ambient water.

The response of  $\text{CaCO}_3$  sediments to elevated carbon concentration.

On the microscale: The fascinating complexities of hydrate formation and dissolution.

Make "the world" understand that these topics need to be addressed now.