

# Hydrodynamically constrained flux of in situ generated methane hydrate dissolving into undersaturated seawater

Niko Bigalke<sup>1</sup>, Giselher Gust<sup>2</sup>, Gregor Rehder<sup>3</sup>, Andreas Meyer<sup>2</sup>

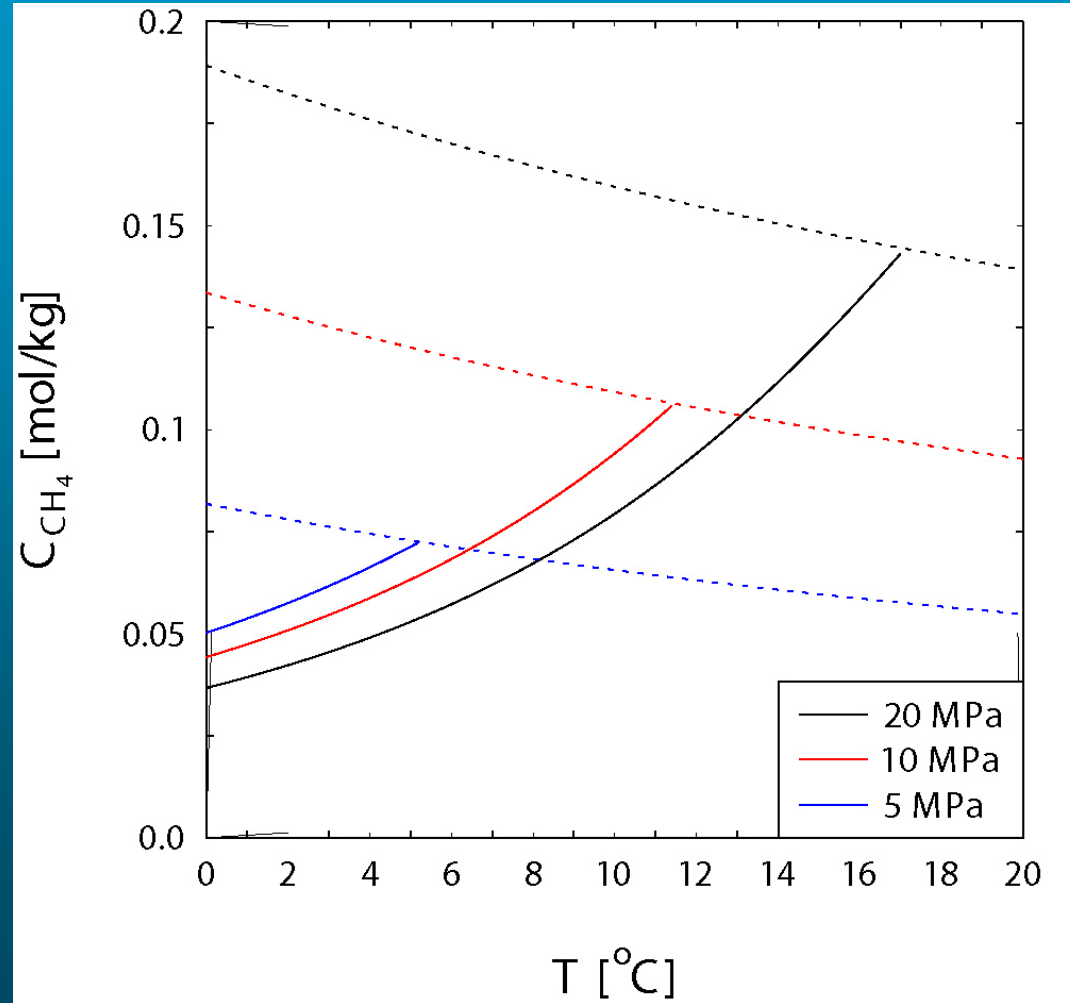
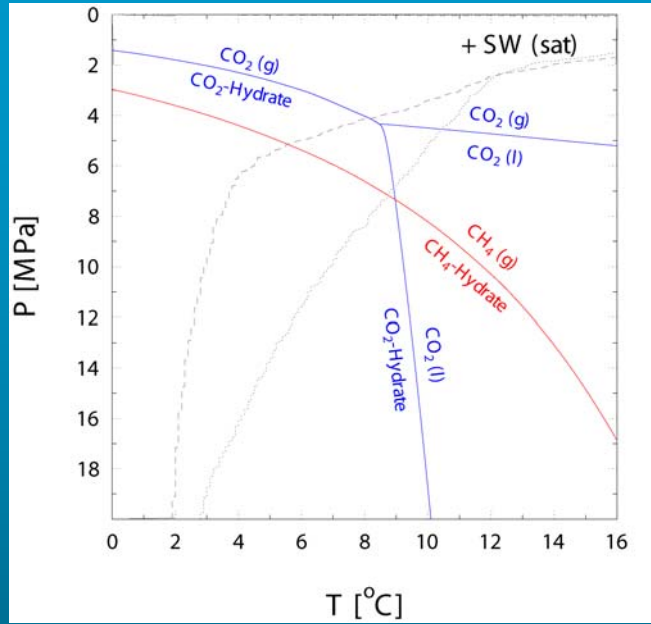
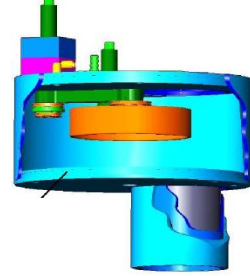
<sup>1</sup>Leibniz Institute of Marine Sciences, IfM-GEOMAR, Kiel, Germany

<sup>2</sup>Technical University Hamburg-Harburg, Dept. of Ocean Engineering,  
Hamburg, Germany

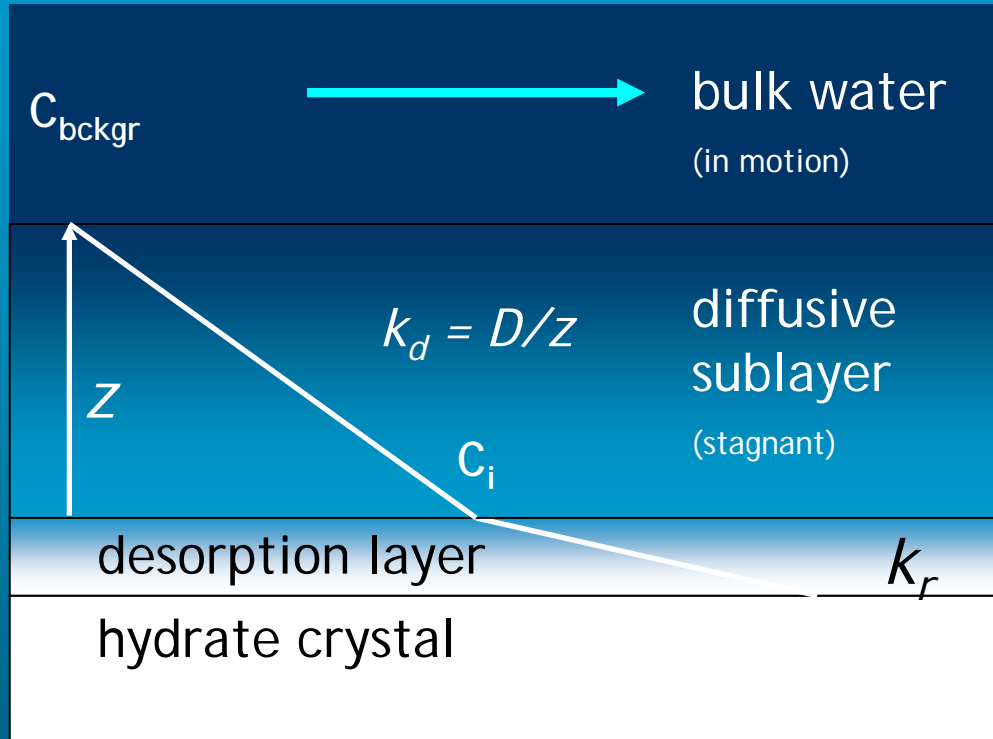
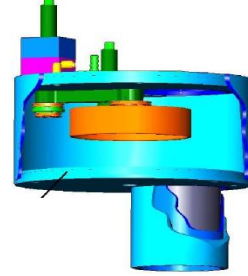
<sup>3</sup>Baltic Sea Research Institute Warnemünde, Rostock, Germany



# Hydrate stability in seawater



# Dissolution of hydrate - diffusion or reaction controlled ?



Concentration

$$F = K' A (C_{sat} - C_{bckgr})$$

$$\frac{1}{K'} = \frac{1}{k_d} + \frac{1}{k_r}$$

reaction controlled:

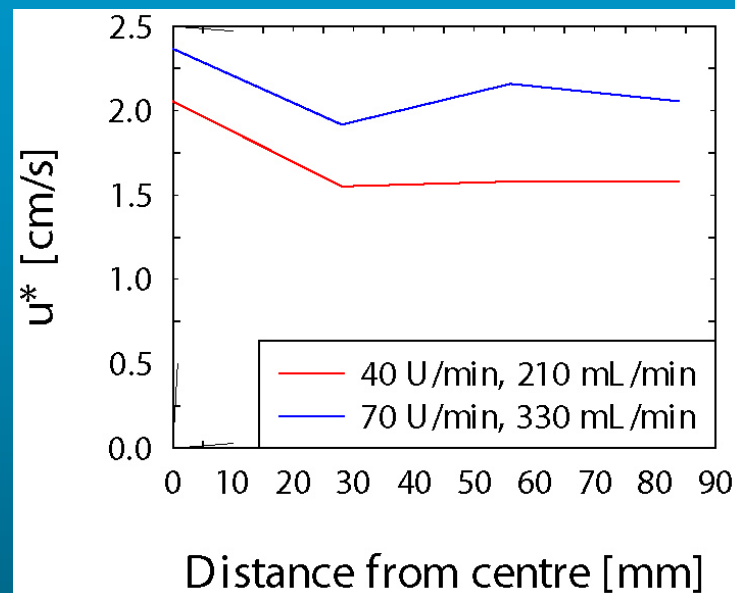
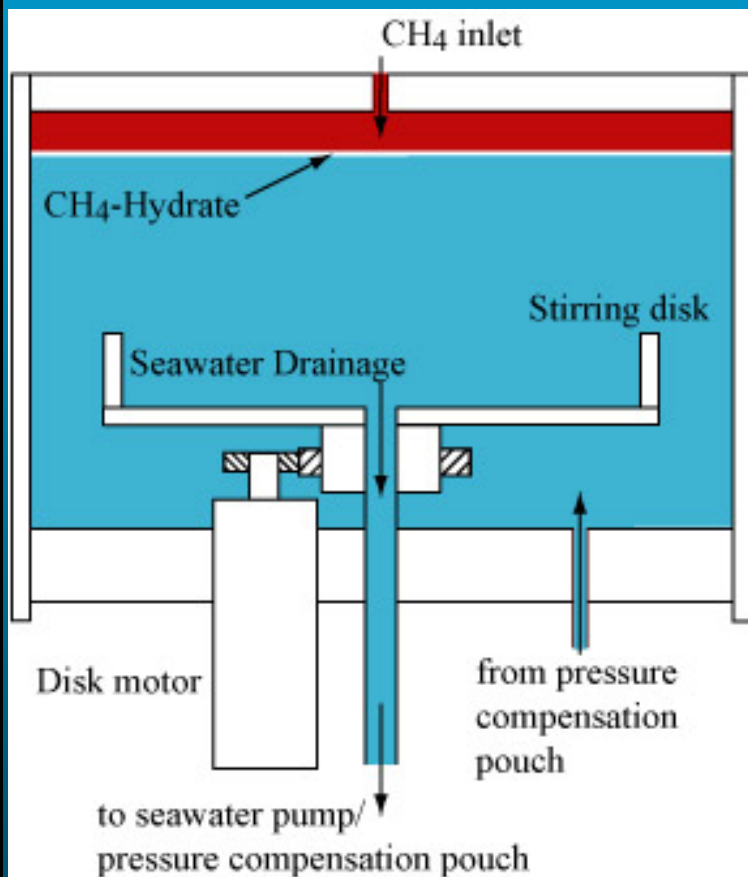
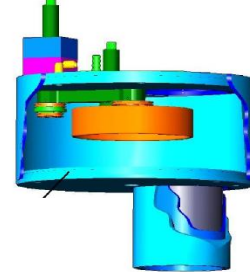
$$K' = k_r$$

diffusion controlled:

$$K' = k_d$$

# Hydrate dissolution - Tools

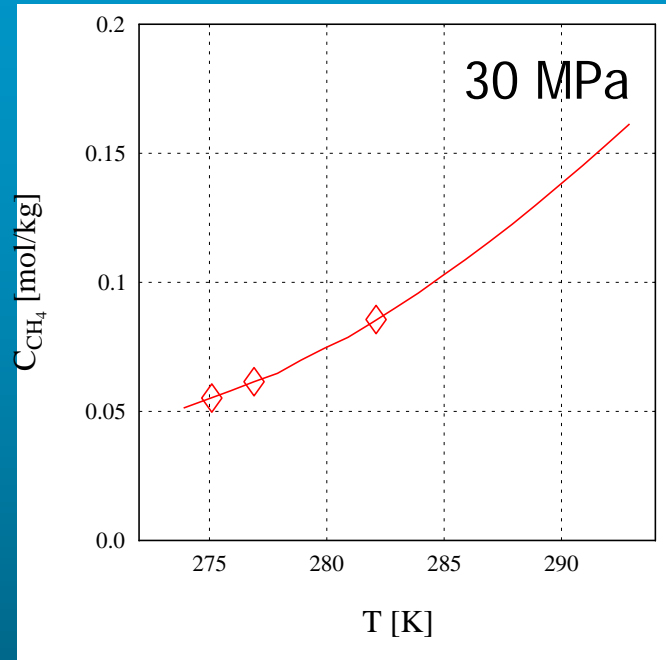
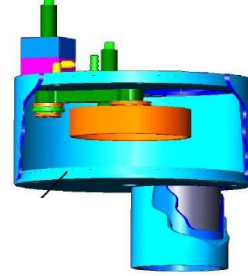
## Interfacial flux chamber „microcosm“



Peppe et al. (1999)

- Production of a radial flowfield at the hydrate/seawater interface in the flux chamber
- Almost constant, adjustable and calibrated friction velocity ( $u^*$ ) over the entire surface

# Hydrate dissolution - Exptl. Parameters

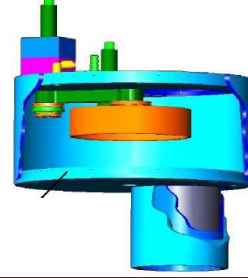


$T$ [°C]	$\rho$ [kg/m <sup>3</sup> ]	$\mu$ [mPas]	$D/10^{-5}$ [cm <sup>2</sup> /s]	$C_{sat}$ [mmol/kg]
2.0	1042	1.726	9.306	55.3 (209.9)
3.7	1041	1.638	9.859	61.4 (204.4)
9.0	1040	1.408	11.53	85.8 (189.4)

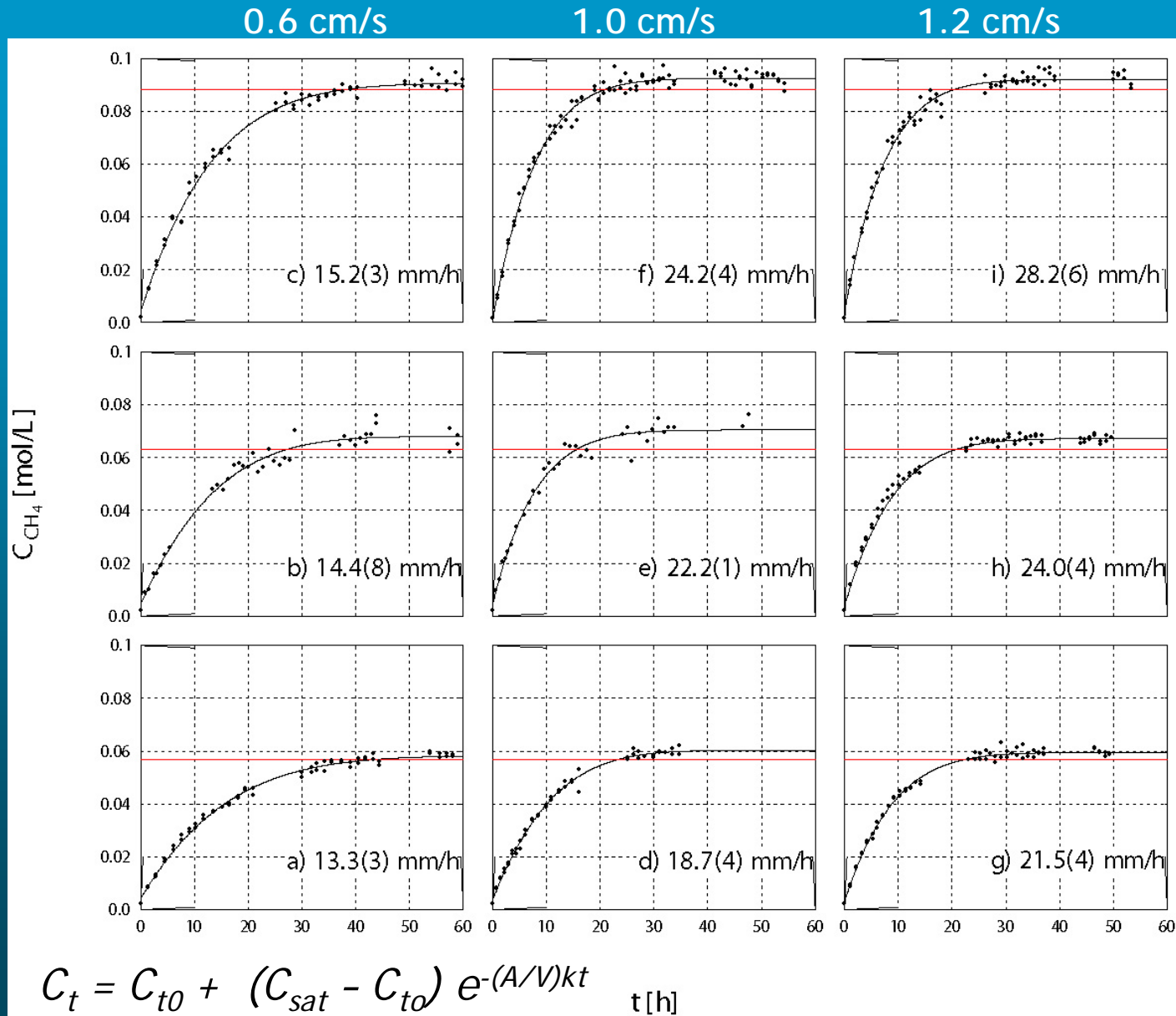
$C_{sat}$ : Tishchenko et al. (2005)

Friction velocities were set to 0.6, 1.0 and 1.2 cm/s for each temperature

# Hydrate dissolution - Results I



Hydrate dissolution at controlled hydrodynamic forcing: Results

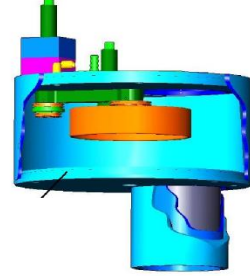


9.0 °C

3.7 °C

2.0 °C

# Hydrate dissolution - Results II

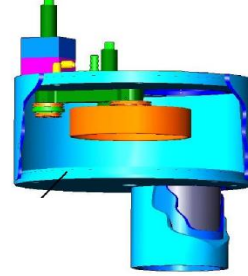


- Saturation concentration in good agreement with predictions according to Tishchenko et al. (2005)
- Change in T results in change of saturation concentration and thus, thermodynamic driving force of dissolution
- Friction velocity ( $u^*$ ) has a strong impact on the dissolution rate

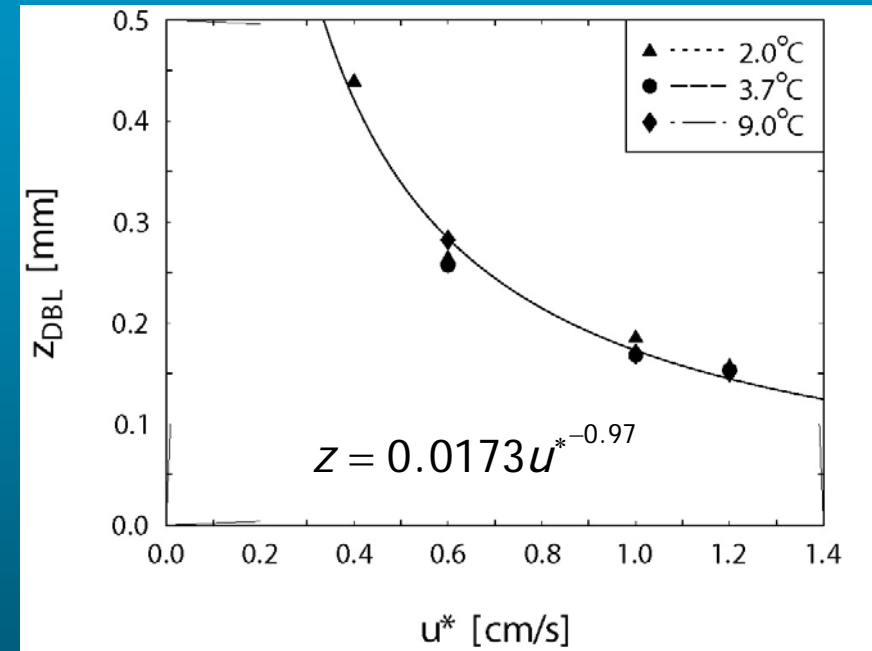
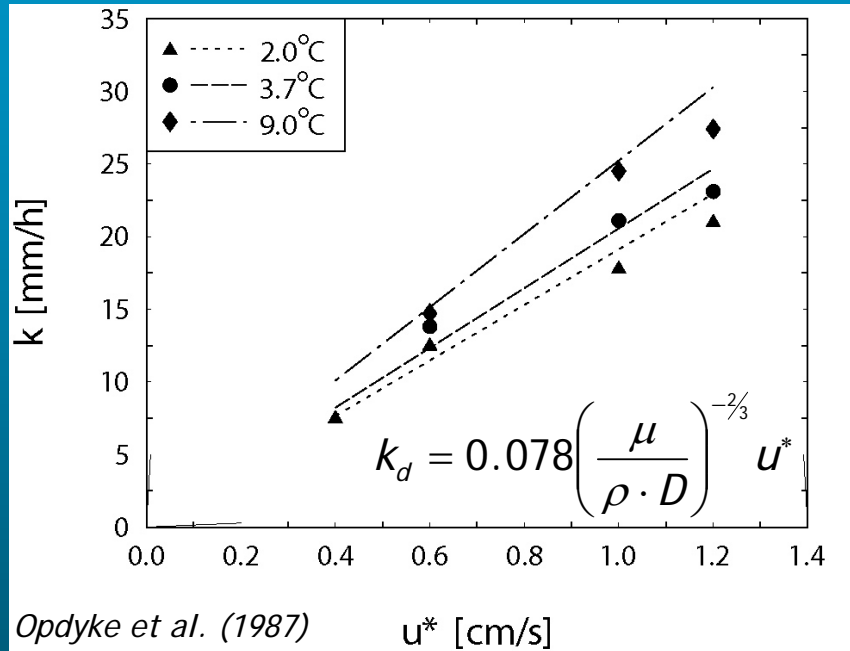
$$\frac{1}{K'} = \frac{1}{k_d} \quad \frac{dn}{dt} = k_d A (C_{sat} - C_{bckgr})$$

- Results strongly substantiate idea dissolution of methane hydrate in undersaturated seawater is a diffusion-controlled process

# Hydrate dissolution - Results III



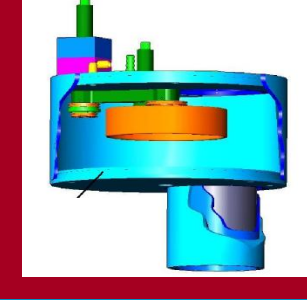
$$k_d = D/z$$



- Excellent agreement of measured transfer coefficients and those obtained from the dissolution of smooth alabaster plates demonstrates reliability of our data.
- Data yield a correlation for the flux of methane from decomposing hydrate outcrops for a broad range of  $P$ ,  $T$  and  $u^*$  conditions prevailing in the oceans on the seafloor



# Comparison with earlier data



current speed: 1.6 cm/s ->

$$u^* = 0.07 \text{ cm/s}$$

$$D = 10^{-5} \text{ cm}^2/\text{s}$$

$T, P, C_{\text{sat}} = ?$   
 $z = 1 \text{ mm}$

$T = 0^\circ\text{C}$   
 $P = 12 \text{ MPa}$   
 $C_{\text{sat}} = 53.7 \text{ mmol/L}$   
 $z = 2.3 \text{ mm}$

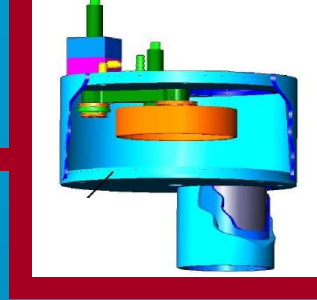


Egorov et al. (1999)



this study

# Comparison with earlier data



current speed: 1.6 cm/s ->

$u^* = 0.07 \text{ cm/s}$

$D = 10^{-5} \text{ cm}^2/\text{s}$

current speed: ? ->

$u^* = ?$

$T = 3.5^\circ\text{C}$

$P = 10.5 \text{ MPa}$

$C_{\text{sat}} = 69.8 \text{ mmol/L}$

$D = 10^{-5} \text{ cm}^2/\text{s}$

$T, P, C_{\text{sat}} = ?$   
 $z = 1 \text{ mm}$

$T = 0^\circ\text{C}$   
 $P = 12 \text{ MPa}$   
 $C_{\text{sat}} = 53.7 \text{ mmol/L}$   
 $z = 2.3 \text{ mm}$

$z = ?$

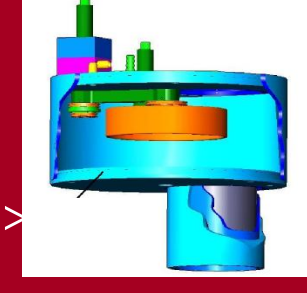


Egorov et al. (1999)

this study

Rehder et al. (2004)

# Comparison with earlier data



current speed: 1.6 cm/s ->

$u^* = 0.07$  cm/s

$D = 10^{-5}$  cm<sup>2</sup>/s

current speed: 1.75 cm/s ->

$u^* = 0.08$  cm/s

Hester et al.,  
pers. comm.

$T = 3.5^\circ\text{C}$

$P = 10.5$  MPa

$C_{\text{sat}} = 69.8$  mmol/L

$D = 10^{-5}$  cm<sup>2</sup>/s

$T, P, C_{\text{sat}} = ?$   
 $z = 1$  mm

$T = 0^\circ\text{C}$   
 $P = 12$  MPa  
 $C_{\text{sat}} = 53.7$  mmol/L  
 $z = 2.3$  mm

$z = 0.179$  mm

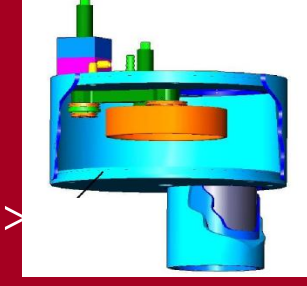


Egorov et al. (1999)

this study

Rehder et al. (2004)

# Comparison with earlier data



current speed: 1.6 cm/s ->

$u^* = 0.07$  cm/s

$D = 10^{-5}$  cm<sup>2</sup>/s

current speed: 1.75 cm/s ->

$u^* = 0.08$  cm/s

Hester et al.,  
pers. comm.

$T = 3.5^\circ\text{C}$

$P = 10.5$  MPa

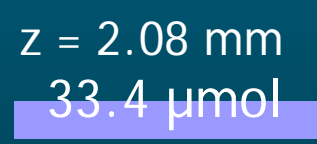
$C_{\text{sat}} = 69.8$  mmol/L

$D = 10^{-5}$  cm<sup>2</sup>/s

$T, P, C_{\text{sat}} = ?$   
 $z = 1$  mm

$T = 0^\circ\text{C}$   
 $P = 12$  MPa  
 $C_{\text{sat}} = 53.7$  mmol/L  
 $z = 2.3$  mm

$z = 0.179$  mm



Egorov et al. (1999)

this study

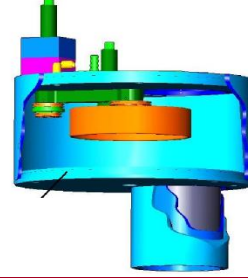
Rehder et al. (2004)

this study

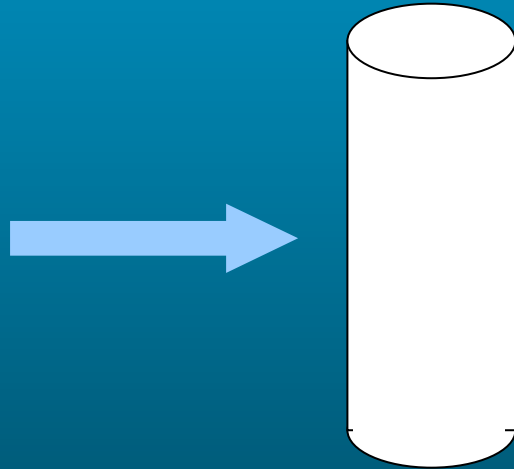
$z = 2.08$  mm

33.4 μmol

# Comparison with earlier data



Ocean experiment:



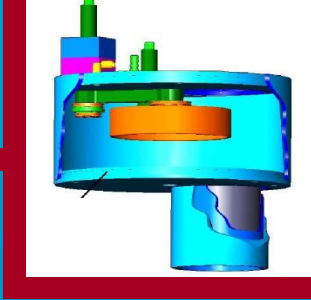
cylindrical hydrate specimens in cross flow

Lab:



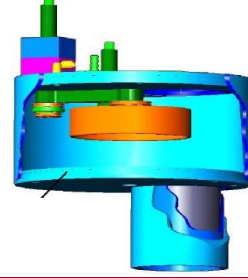
plain surfaces in parallel flow

# Conclusion/outlook

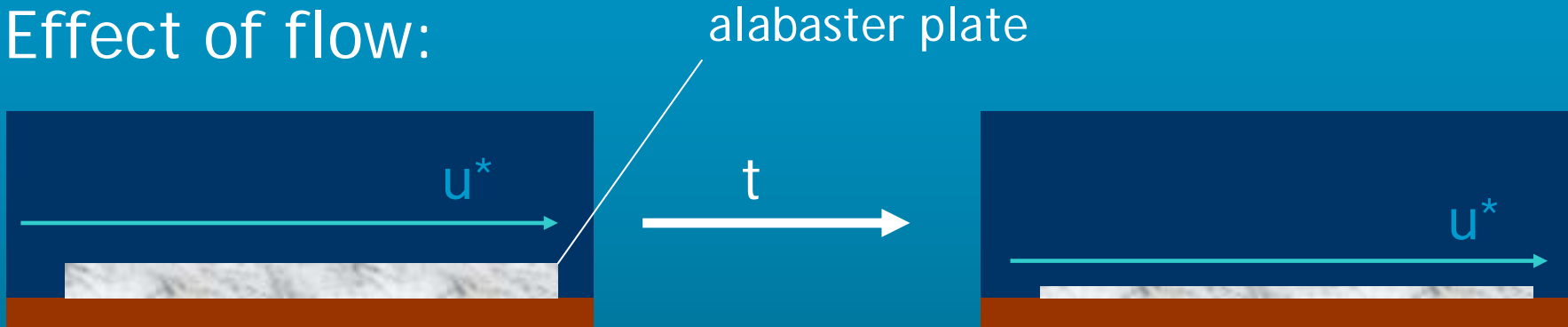


- Dissolution experiments demonstrate that hydrate dissolution in undersaturated seawater at  $P$ -/ $T$ -conditions within the HSF is diffusion and not reaction controlled.
- Based on the experimental data, a  $k_d/u^*$  correlation was obtained, which excellently agrees with and is thus validated by an earlier correlation obtained from dissolution experiments with alabaster plates.
- The validated correlation permits an accurate prediction of the dissolution rates of smooth and clean methane hydrates exposed to a flow of undersaturated seawater for a broad range of oceanic conditions.
- Comparison with earlier data and postulations shows significant discrepancies. In one case this was due to a different sublayer thickness, which for lack of available data has been poorly constrained before.
- Future studies should address the role of inhibitors such as sediments or bacterial mats covering most natural gas hydrates.

# Relevant Experiments I

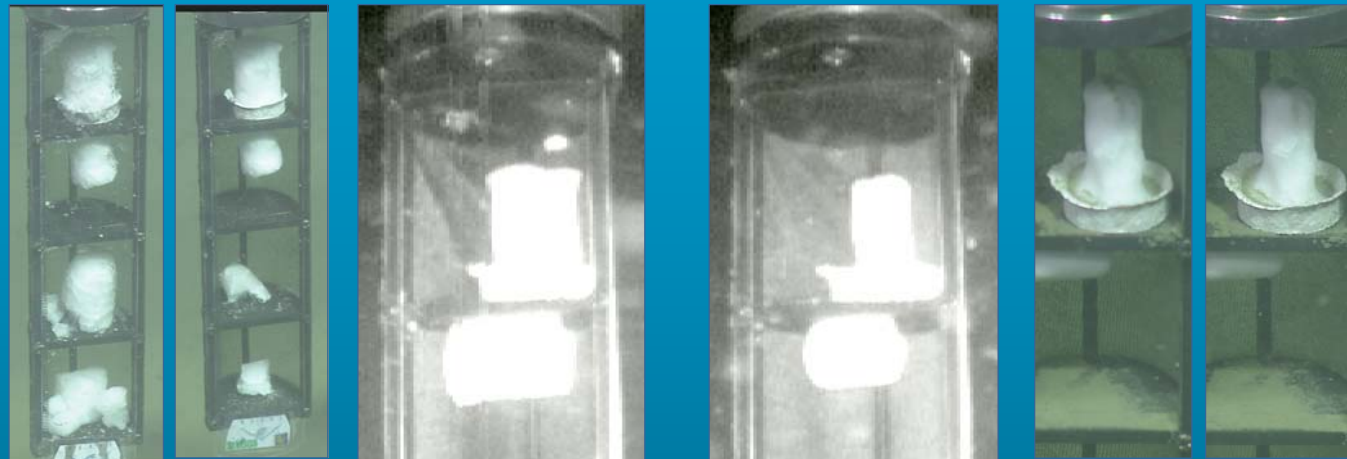
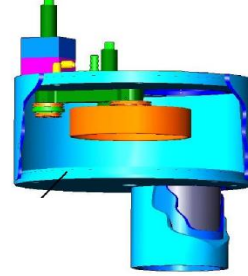


Effect of flow:



- Flux of Ca and  $\text{SO}_4$  determined from mass loss of the alabaster
- A diffusive boundary layer model was assumed to explain mass loss.
- $k = 0.078 \text{ Sc}^{-2/3} u^*$

# Relevant Experiments II



2h:19min  
HDTV

20h:45min  
Hi8

3h:12min  
HDTV

$$F = D/z (C_{\text{sat}} - C_{t0})$$

$$z(\text{CO}_2) = z(\text{CH}_4),$$

$$D(\text{CO}_2) = D(\text{CH}_4),$$

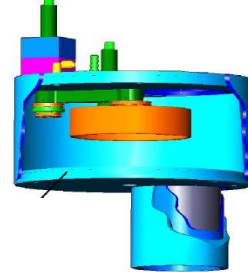
$$C_{t0} = 0$$

$$F(\text{CO}_2)/F(\text{CH}_4) = C_{\text{sat}}(\text{CO}_2)/C_{\text{sat}}(\text{CH}_4)$$

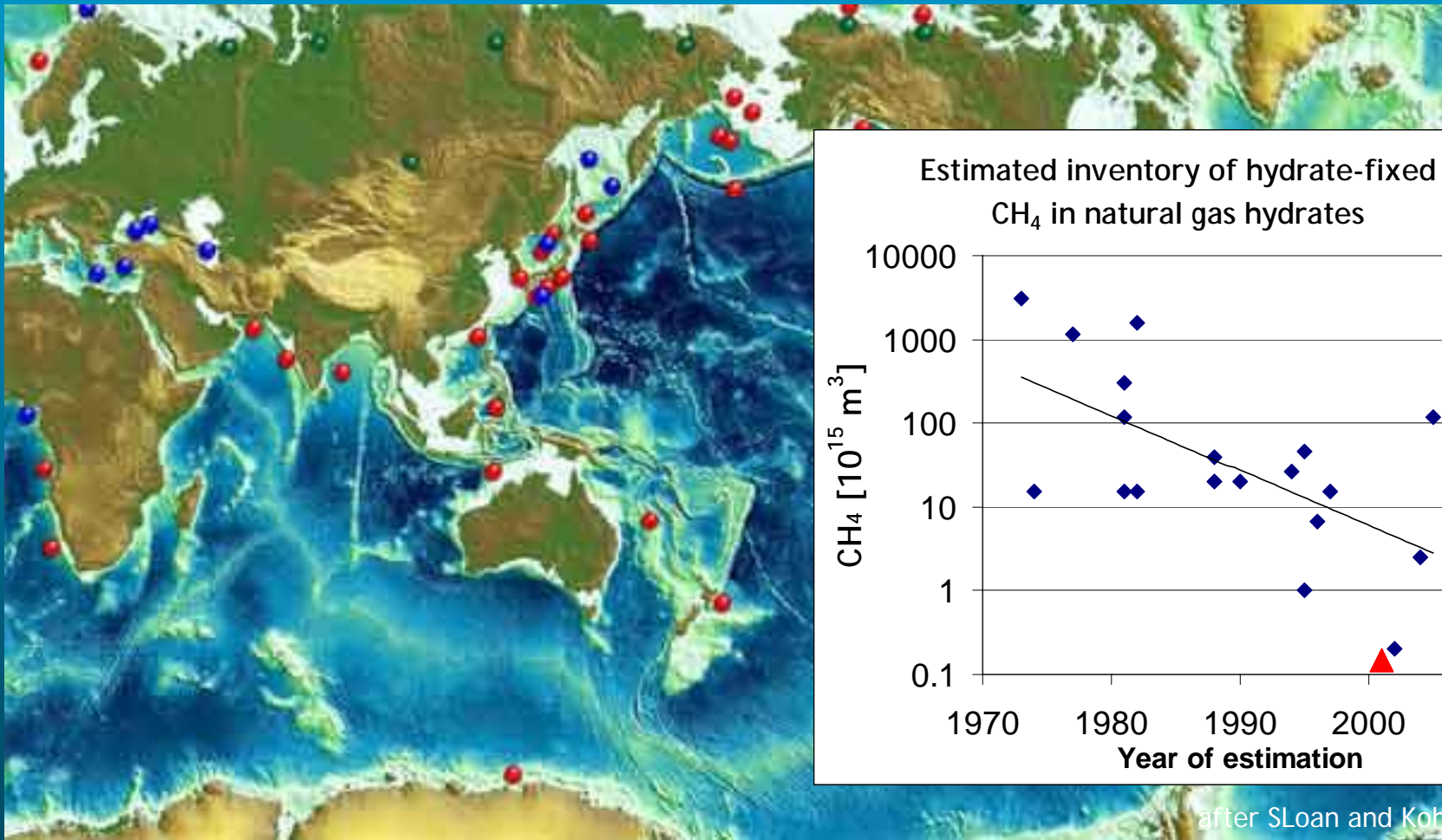
- Results of the field experiment fit well into a diffusive boundary layer model
- Dissolution of hydrates appears to be diffusion limited, not by kinetics of a chemical reaction



# Idea/Motivation



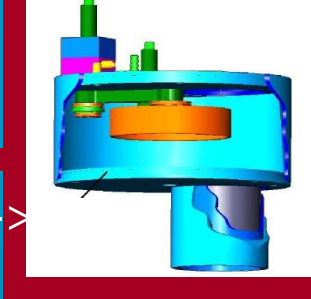
CH4 hydrate dissolution at controlled hydrodynamic forcing



after Sloan and Koh, 2007

J. Greinert, IFM-GEOMAR

# Comparison with earlier data



current speed: 1.6 cm/s ->

$u^* = 0.07$  cm/s

$D = 10^{-5}$  cm<sup>2</sup>/s

$T, P, C_{\text{sat}} = ?$   
 $z = 2.3$  mm

$T = 2.0^\circ\text{C}$

$P = 30$  MPa

$C_{\text{sat}} = 57.6$  mmol/L  
 $z = 2.3$  mm

21.7 m<sup>3</sup>

Egorov et al. (1999)

17.4 m<sup>3</sup>

this study

current speed: 1.75 cm/s ->

$u^* = 0.08$  cm/s

$T = 3.5^\circ\text{C}$

$P = 10.5$  MPa

$C_{\text{sat}} = 69.8$  mmol/L

$D = 10^{-5}$  cm<sup>2</sup>/s

$z_{\text{ocean}}/z_{\text{lab}}$

$=$

$\text{Flux}_{\text{lab}}/\text{Flux}_{\text{ocean}}$

$z_{\text{ocean}}/z_{\text{lab}} = 11.6$

$\text{Flux}_{\text{lab}}/\text{Flux}_{\text{ocean}} = 11.1$

$z = 2.08$  mm

33.4  $\mu\text{mol}$

this study

$z = 0.089$  mm

37.6  $\mu\text{mol}$

Rehder et al. (2004)

CH<sub>4</sub> hydrate dissolution at controlled hydrodynamic forcing