# Untersuchungen zu Gashydraten

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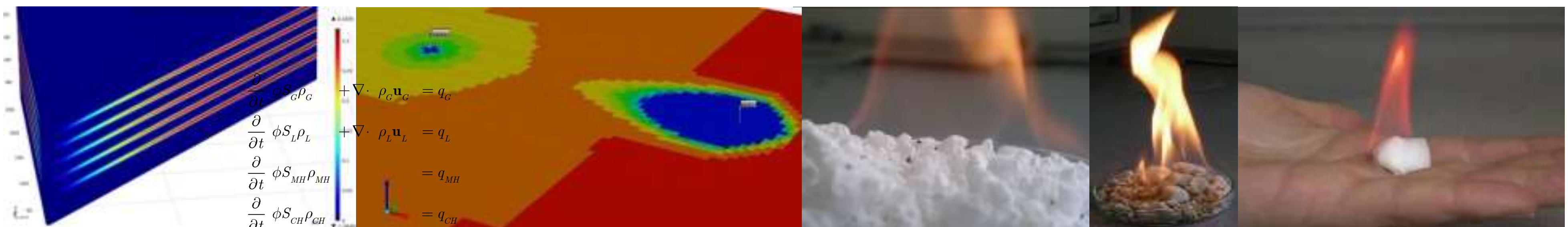


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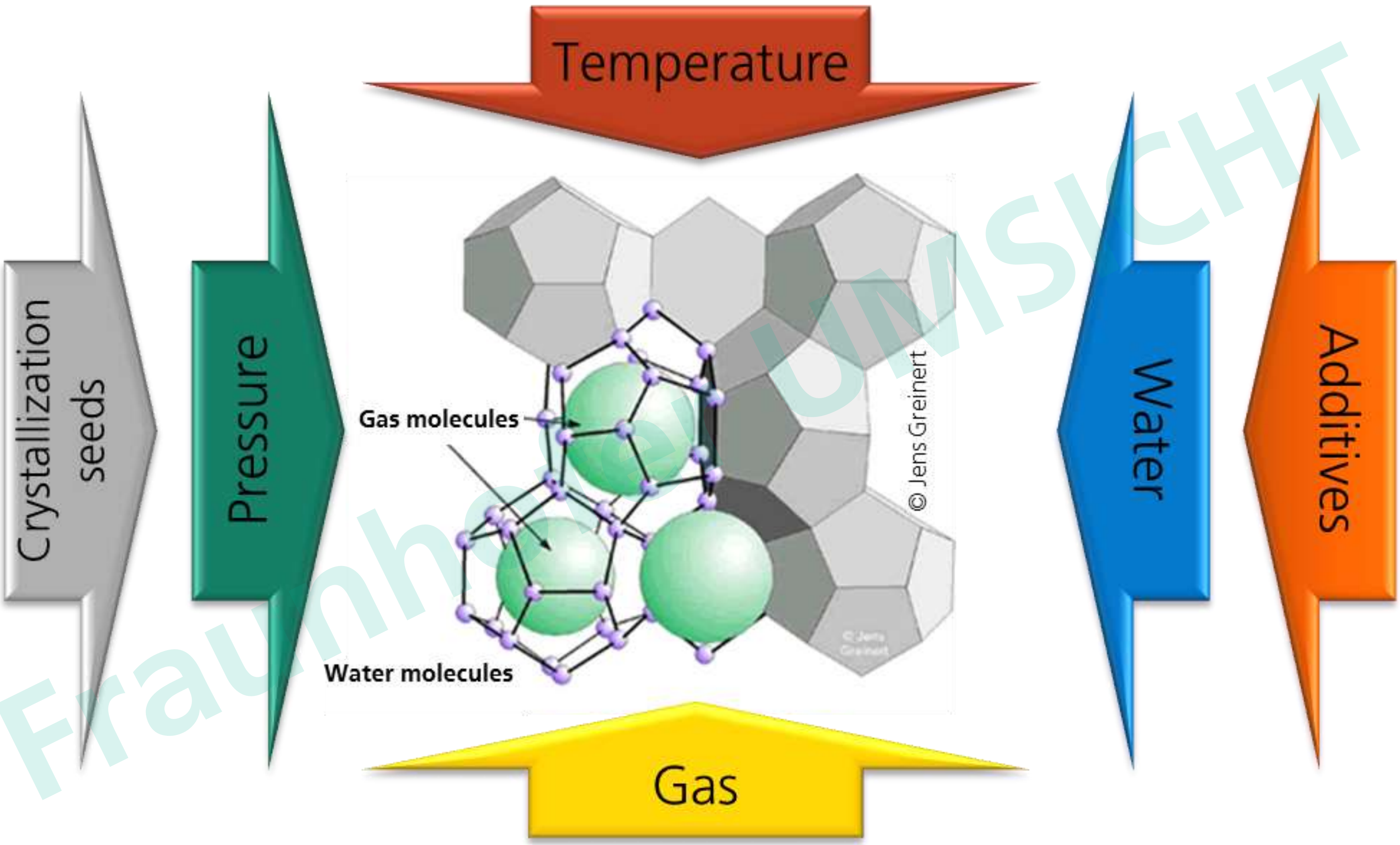
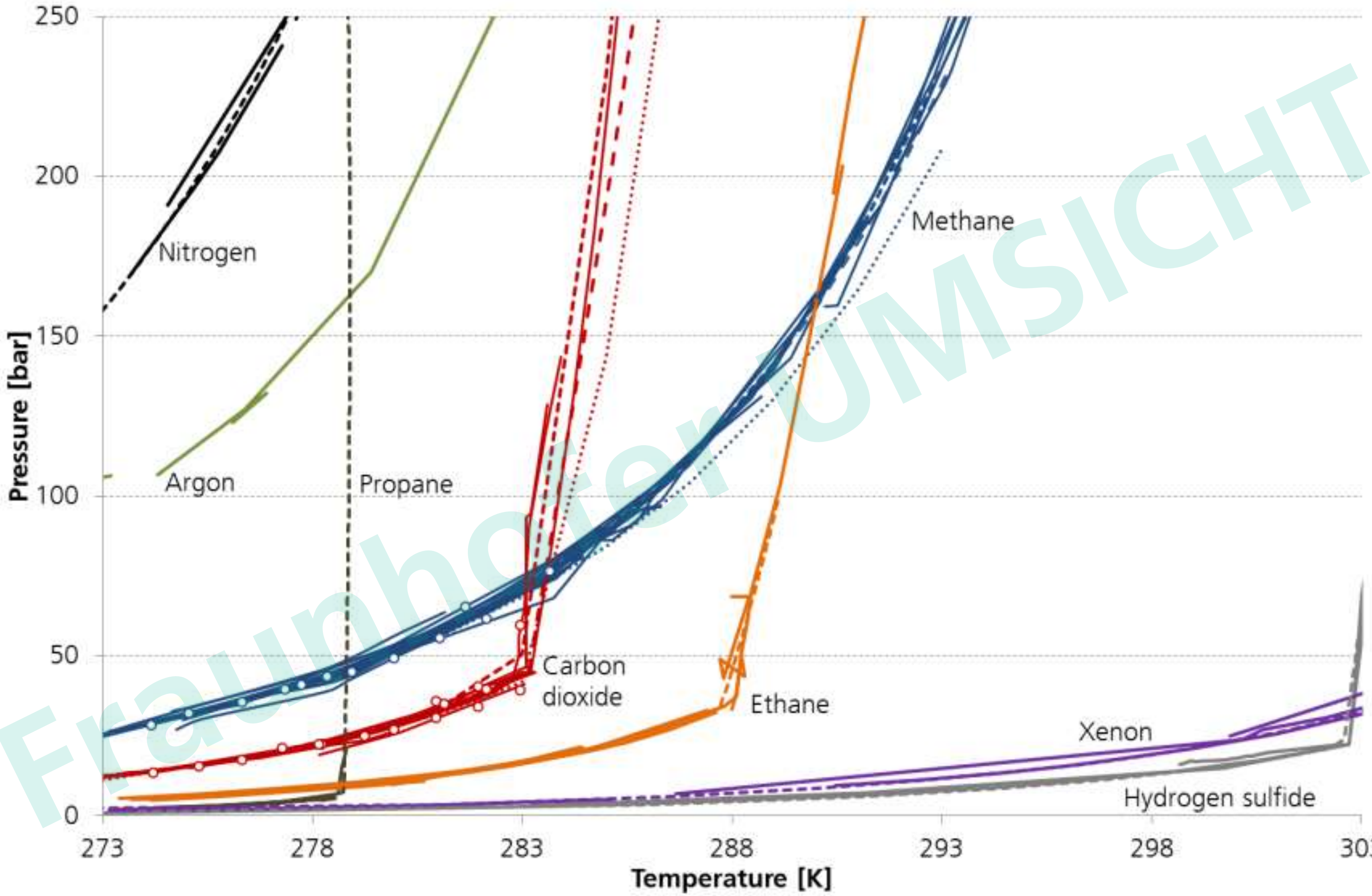
# Outline

- Introduction to gas hydrates
- Applications of gas hydrates
- Use of additives to enhance gas hydrate formation
  Experiments & results
- Summary

# What are gas hydrates?

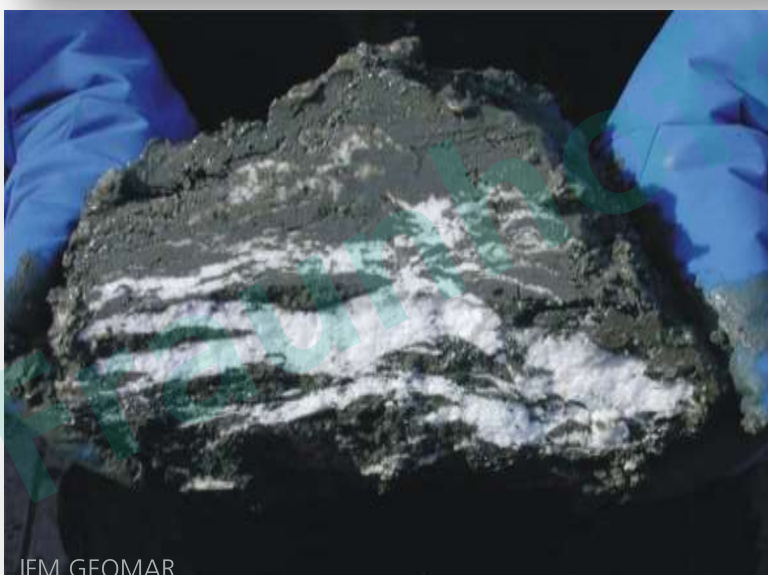


# Stability of gas hydrates



# How do gas hydrates look like?









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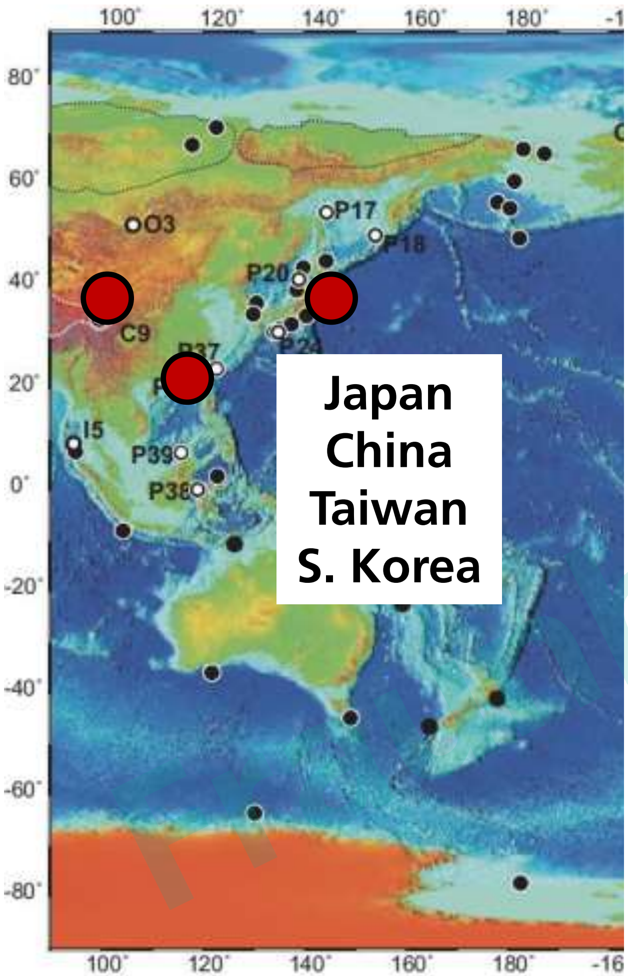
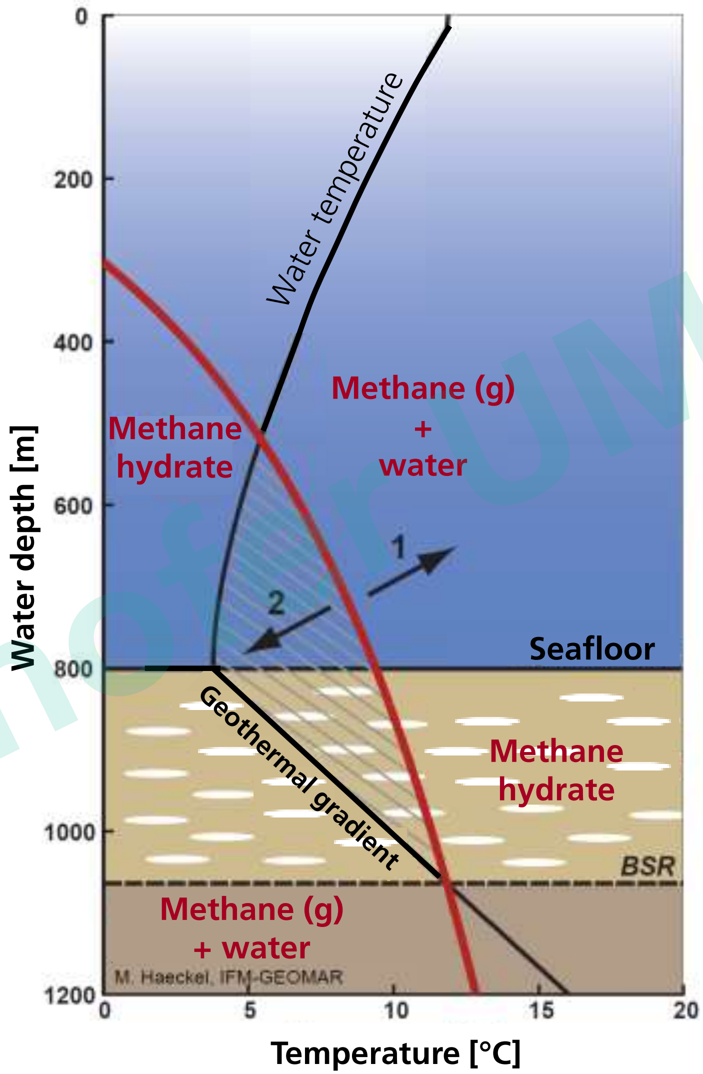
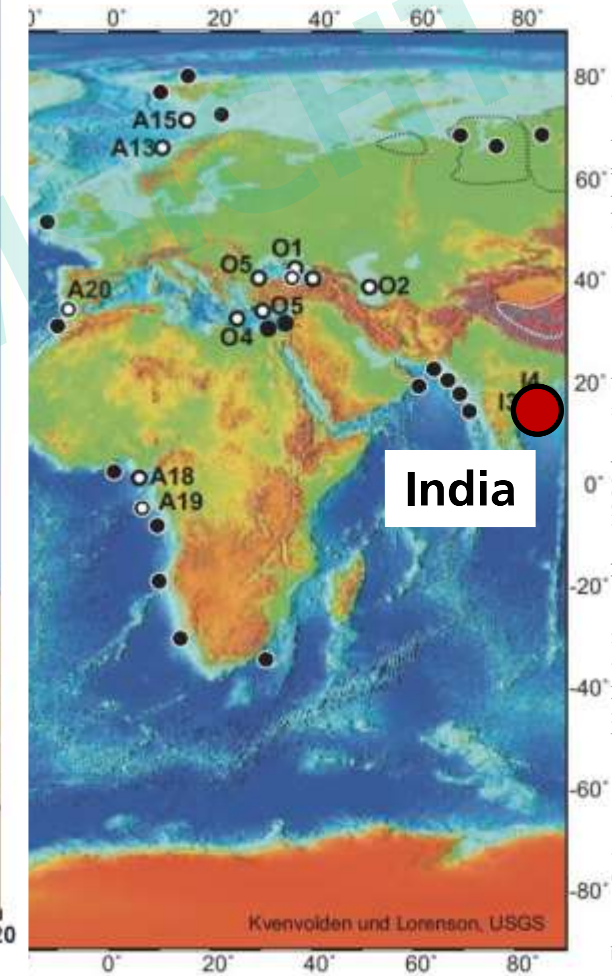
# Where you can find hydrates?



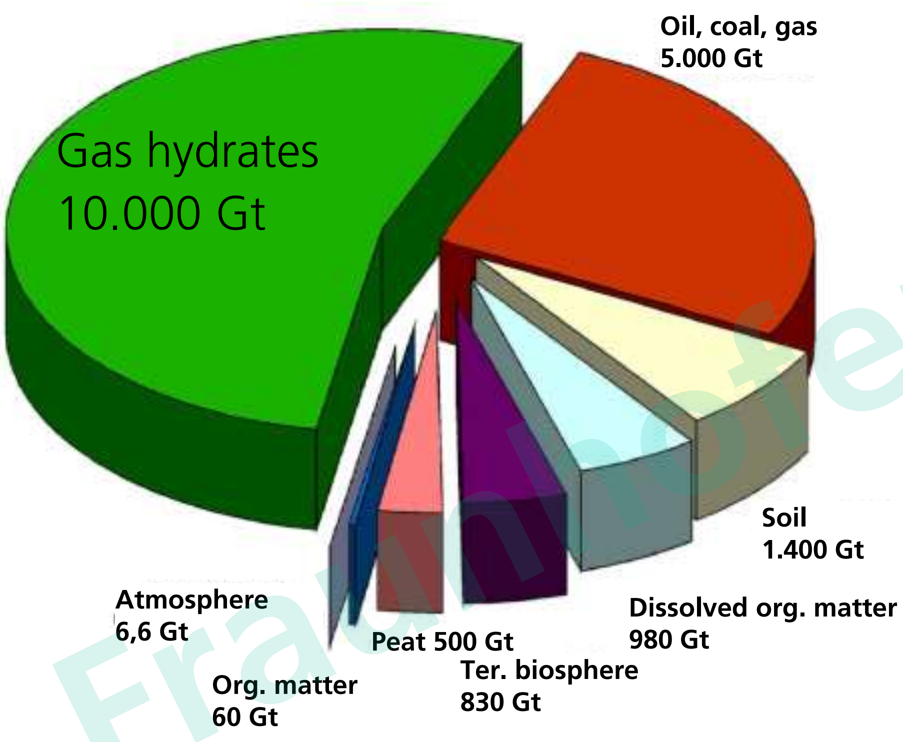




Thomas D. Lorenson und Keith A. Kvenvolden, USGS, http://walrus.wr.usgs.gov/globalhydrate/

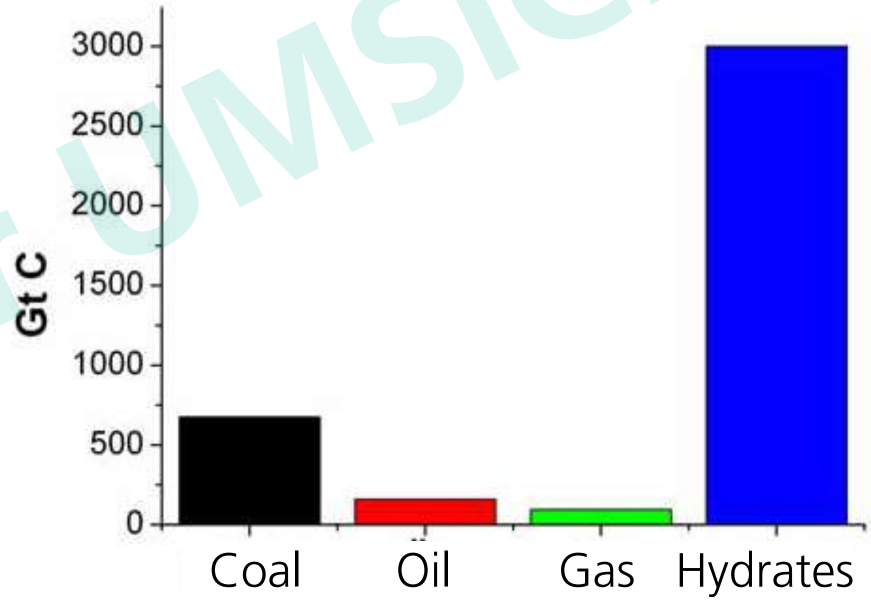
# Gas hydrates and carbon matter

Gas hydrates and carbon matter



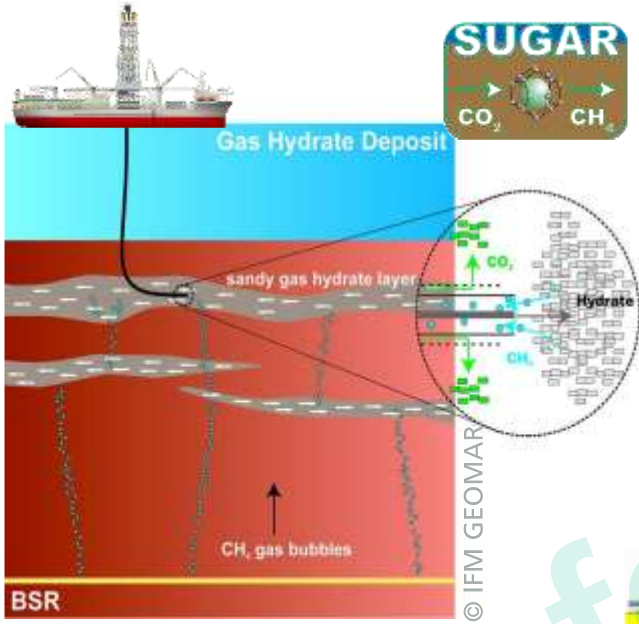

Keith A. Kvenvolden, Methane hydrate – A major reservoir of carbon in the shallow geosphere?, Chem. Geol. 71, 1988

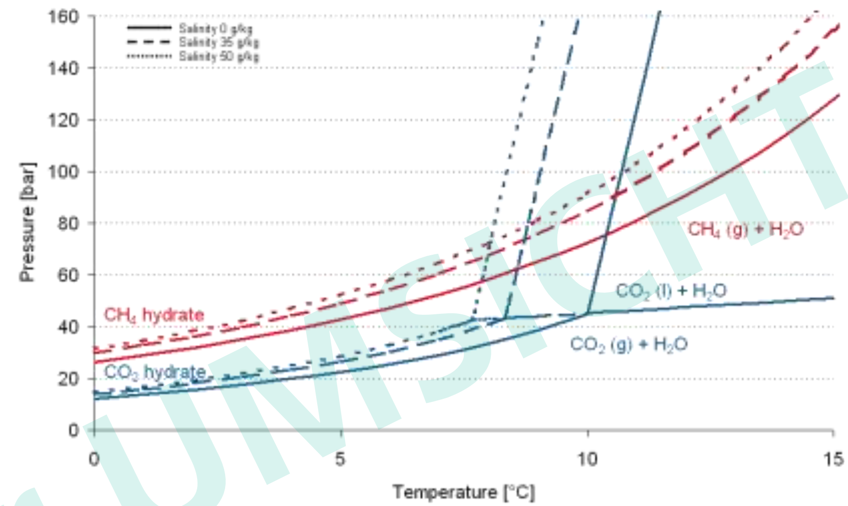
Fossil fuel reserves and submarine gas hydrates



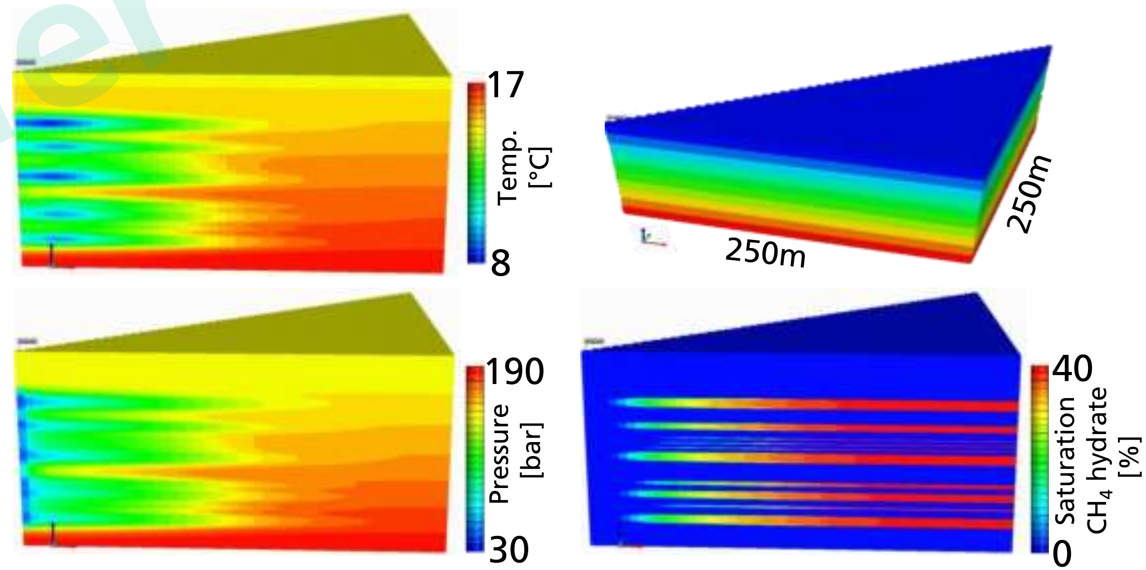

Energy Outlook 2007, Buffett & Archer (2004)

# Simulation of natural gas hydrate exploitation




- $CO_2$ hydrate stable at lower pressure / higher temperature
- $CO_2$ higher stability
- Replacing $CH_4$ by $CO_2$
- Simultaneous production of $CH_4$ and storage of $CO_2$
- Sustainable energy supply system




t = 15 months

# Applications of gas hydrates

- **Storage** of natural gas, $H_2$ and $CO_2$ (sequestration)
- **Transport** of $CH_4$ as an alternative to LNG, CNG or pipeline
- **Separation** of $CO_2$ / $H_2S$ / $N_2$ / $H_2$ from flue gases and $CH_4$ from biogas as substitution of adsorption processes
- **Water purification** for sea water desalination, removal of toxic agents and pollutants as an alternative to distillation or membranes
- **Cooling energy storage** (in slurries) as latent heat (phase change material) for air conditioning
- Gas compression, treatment of food, biotechnology



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# Additives for gas hydrates

may have an impact on **thermodynamics, kinetics, physical-chemical properties** of the gas hydrate system, and are used as:

- **Inhibitors** to prevent gas hydrate formation

  - Alcohols or salts (need of high concentrations and elaborate recycling)

  → LDHI → Polymers (ppm) as more efficient and less expensive approach

- **Promotors** for enhancing process efficiency in terms of energy

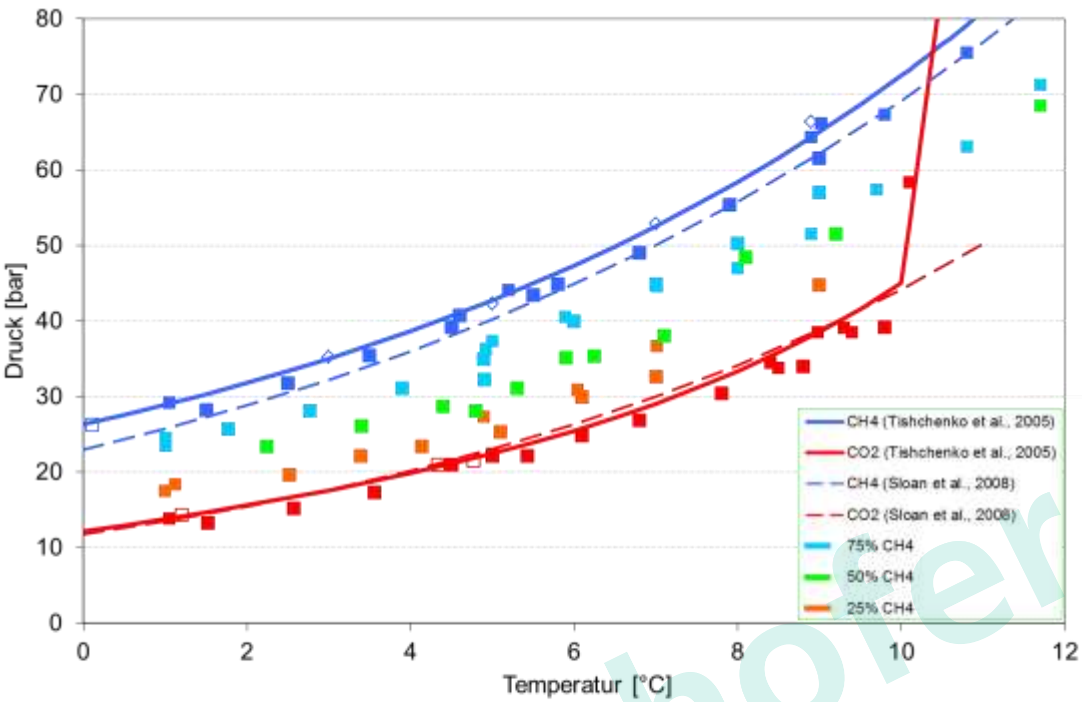
  → e.g. propane, $CO_2$ or THF and TBAB

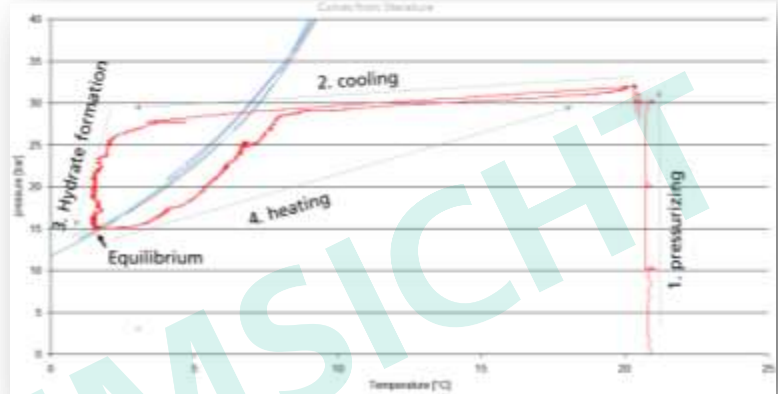
  → Polymers, surfactants (ppm)

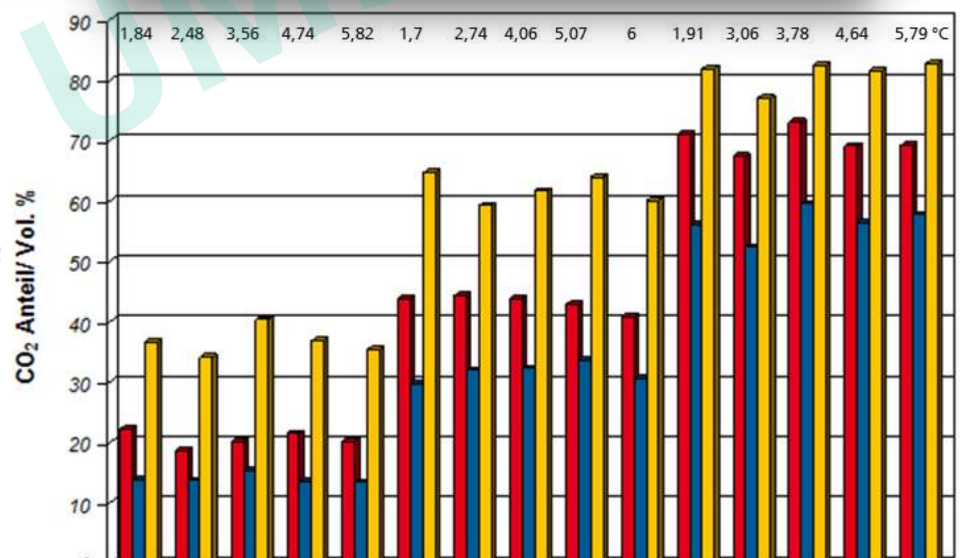
- **Anti-Agglomerants** for prevention of gas hydrate plugging (e.g. pipelines)

LDHI – Low dosage hydrate inhibitors
THF – Tetrahydrofuran
TBAB – Tetra-n-butylammonium bromide

# Phase equilibrium of pure and mixed hydrates



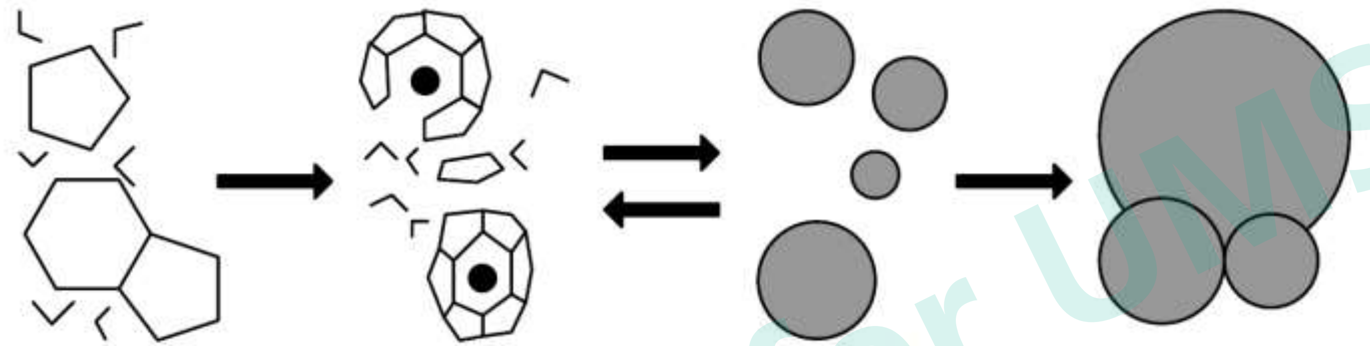

| | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Feedgas (A) | 22,16 | 18,59 | 20,12 | 21,45 | 20,18 | 43,89 | 44,30 | 43,88 | 42,81 | 40,76 | 70,98 | 67,34 | 73,03 | 69,10 | 69,13 |
| Gasphase (B) | 13,68 | 13,65 | 15,26 | 13,56 | 13,35 | 29,74 | 31,89 | 32,20 | 33,7 | 30,49 | 56,12 | 52,33 | 59,53 | 56,39 | 57,66 |
| Hydratphase (C) | 36,57 | 34,11 | 40,31 | 36,85 | 35,33 | 64,62 | 59,23 | 61,60 | 63,95 | 60,03 | 81,89 | 77,05 | 82,46 | 81,57 | 82,64 |

Versuchsnummer

→ Changing hydrate phase equilibrium by adding a hydrate forming gas (e.g. $CO_2$)

→ Gas separation by hydrate formation: concentration of $CO_2$ in gas hydrate

# Kinetic effect of additives on gas hydrate formation

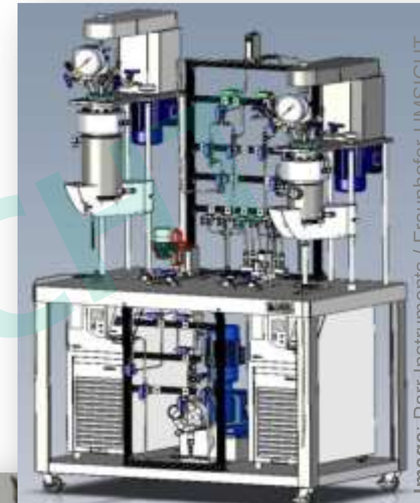


A. Initial condition: Pressure and temperature in hydrate forming region, but no gas molecules dissolved in water.

B. Labile clusters: Upon dissolution of gas in water, labile clusters form immediately.

C. Agglomeration: Labile clusters agglomerate by sharing faces, thus increasing disorder.

D. Primary nucleation and growth: When the size of cluster agglomerate reaches a critical value, growth begins.

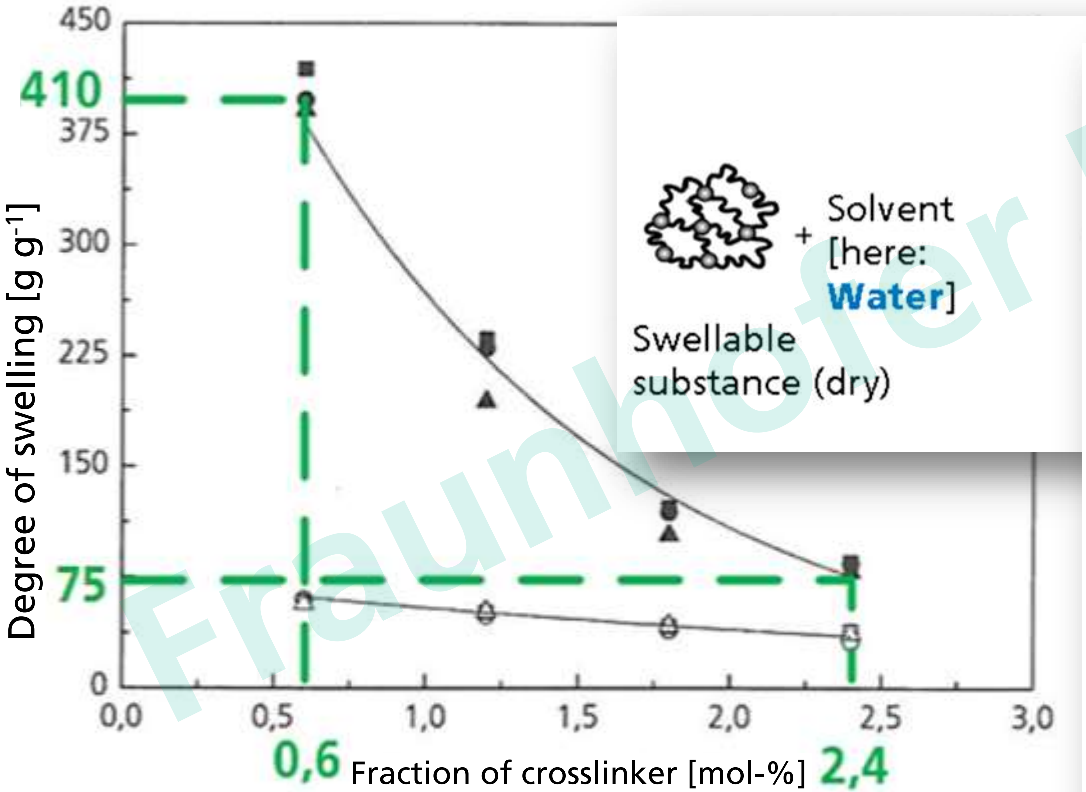


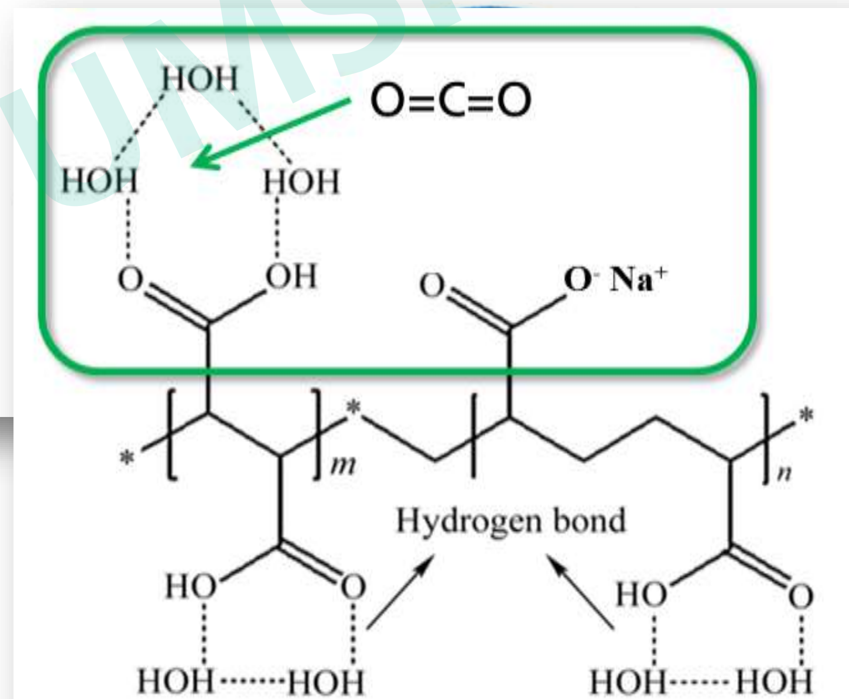



Christiansen et al., 1994

# Additive enhanced $CO_2$ hydrate formation

- Influence on swelling by degree of crosslinking
- Potential hydrogel variables on the $CO_2$ hydrate formation: particle size, **degree of swelling**, chemical structure (ionic character, hydrophobicity), etc.

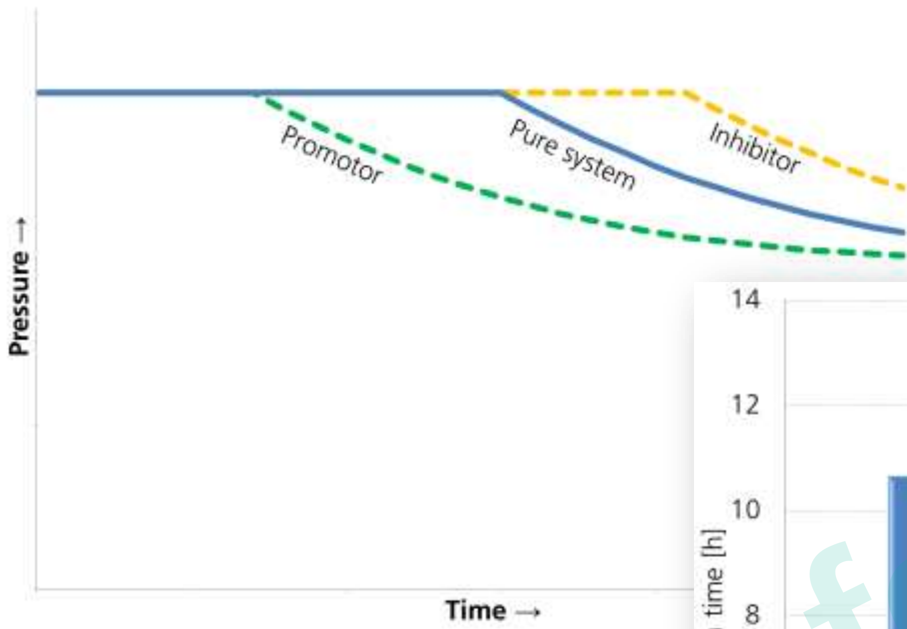



Ring structure formed by SAP and water

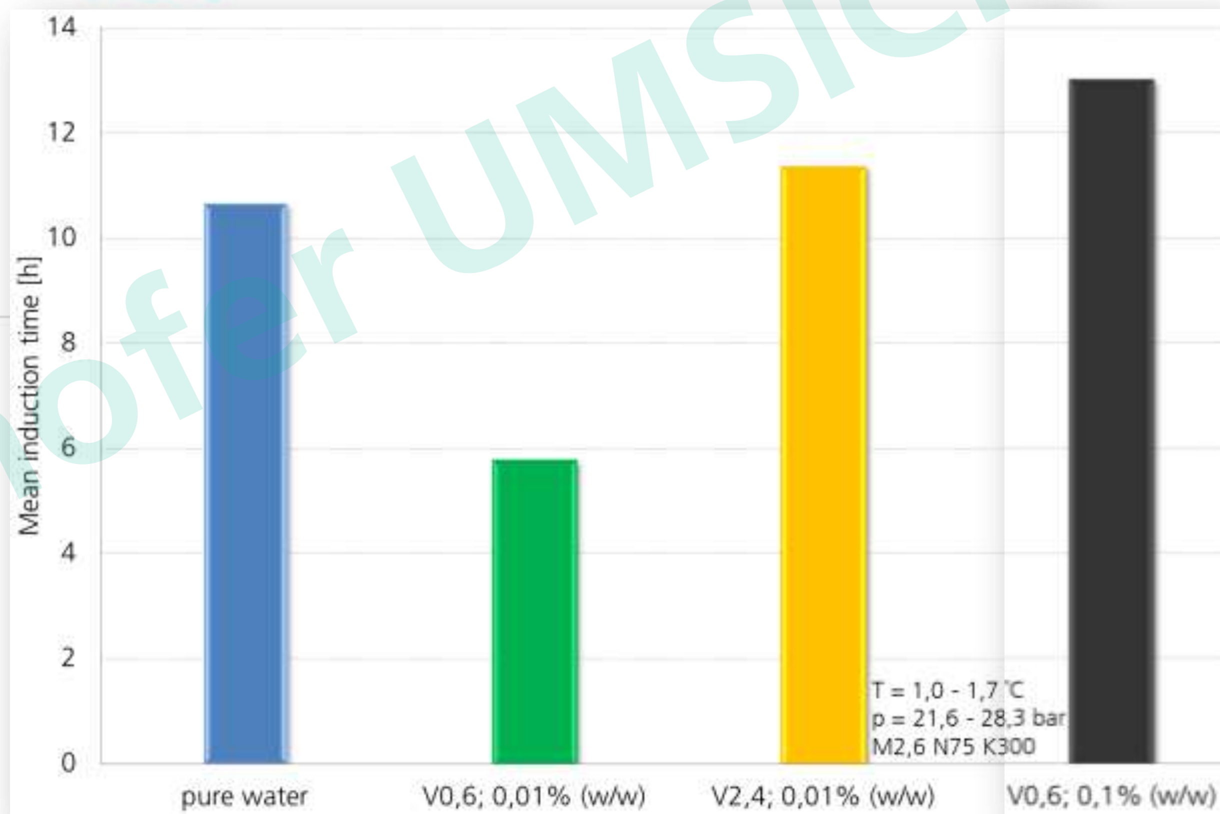
[Wack, 2006 »Zum Quellungsdruck von polymeren Hydrogelen«, PhD-Thesis, figure modified]
[Long et al., 2010 »Promoting effect of super absorbent polymer on hydrate formation«, figure modified]

# Effect of hydrogel on induction time of gas hydrate formation



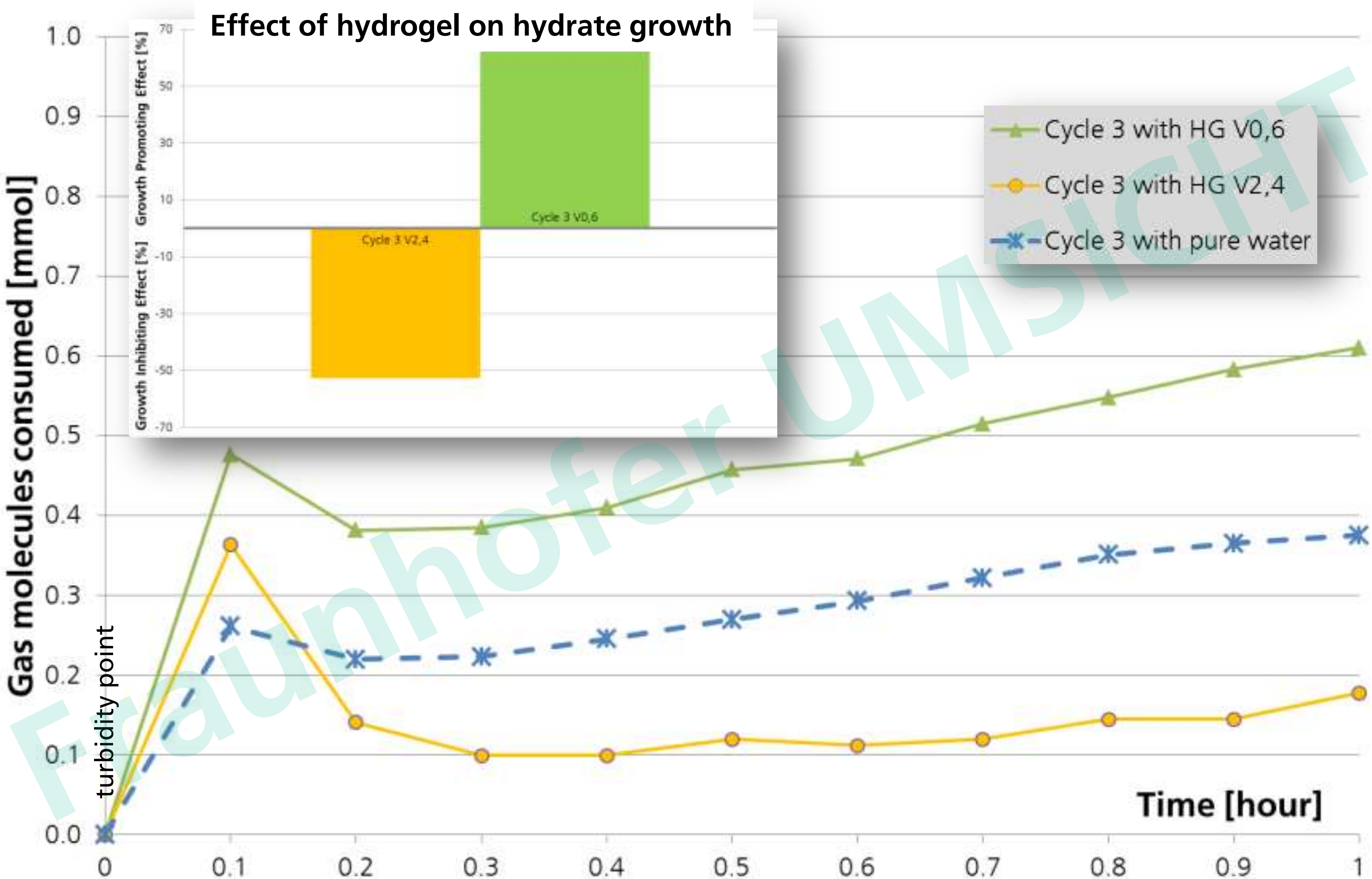

- → Induction time depends on fraction of crosslinker

- → Just small amount of additive is needed to effect induction time




V – Fraction of crosslinker [mol-%]

# Gas consumption during hydrate formation






→ Fraction of crosslinker influences gas consumption

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# Summary

- Various applications of hydrate based technologies exist
  → Natural gas production, $CO_2$ storage, gas separation and cooling energy
- Alternative for "freezing" processes above 0°C
- Additives effecting the thermodynamics, kinetics and physical-chemical properties of gas hydrates
  → Use of polymers (ppm) as process enhancing promoters
  → Tailor-made process
  → Increase of efficiency
- Crosslinking of hydrogels can either have enhancing (V 0,6) or inhibiting (V 2,4) effect on gas hydrate formation
  → V 0,6: shortened induction time; increased gas consumption
  → V 2,4: prolonged induction time; decreased gas consumption
- Large potential but need for further research to understand the occurring mechanisms → Validation of data, screening and scale-up
  → Additional methodical approach by high-pressure DSC

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## Processes

# Thank you for your attention!

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