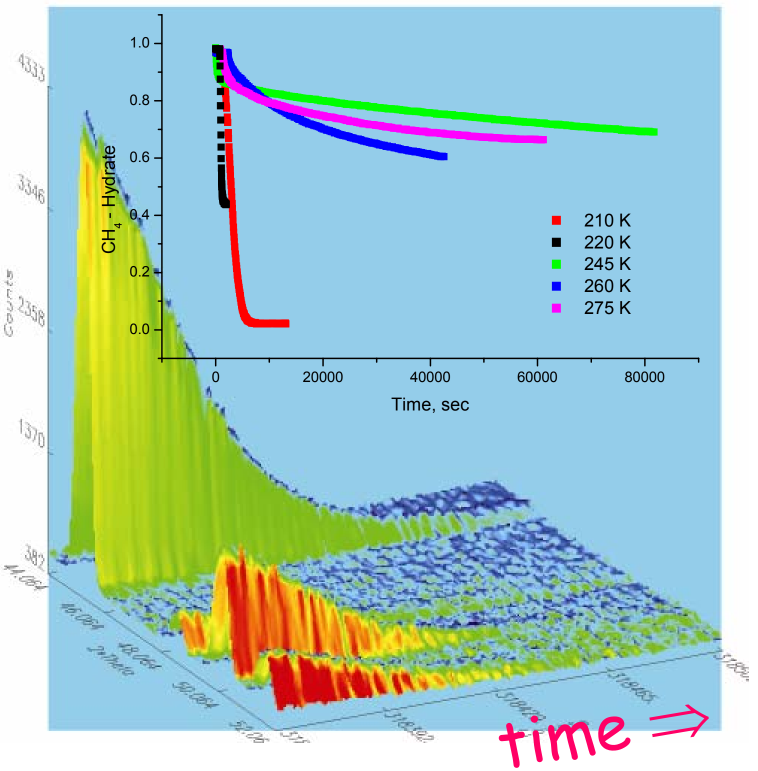
Time resolved neutron diffraction studies with emphasis on water ices and gas hydrates

Werner F. Kuhs
GZG, Kristallographie, University of Göttingen
and **Thomas C. Hansen**
Institut Laue Langevin, Grenoble



Prologue

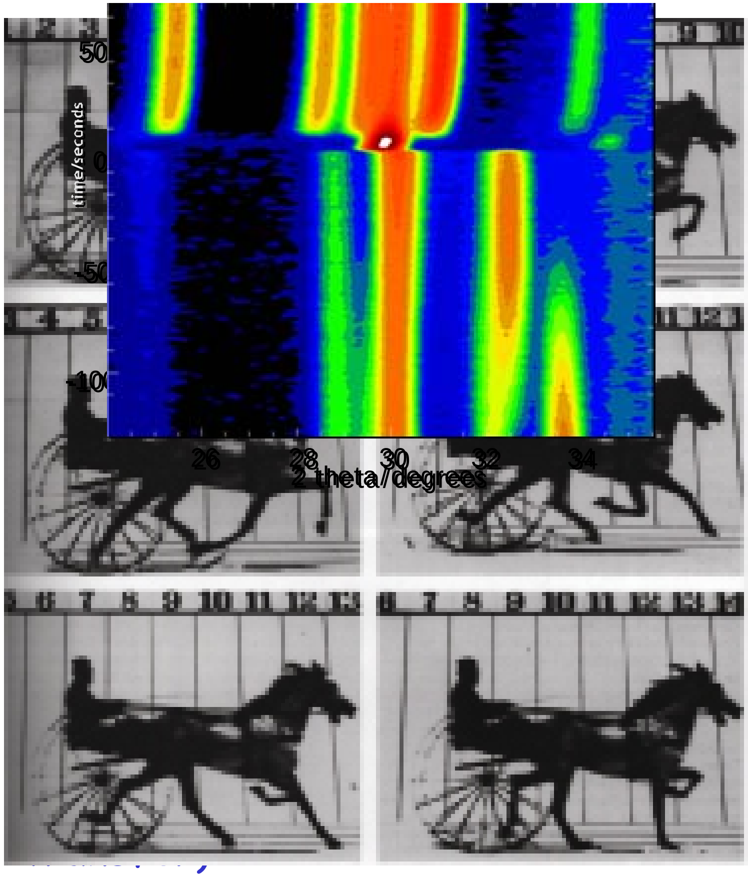
We are living in an ever changing world.

Static structures do not exist; they are conceivable only as a time-space average.

Atoms move around their static positions and show dynamics; the time domain of atomic motion accessible for inelastic scattering is rather short.

The kinetics of chemical reactions (phase and composition changes) and phase transitions (fixed composition) take place over rather extended time domains and can be studies in real-time experiments.

Time resolution



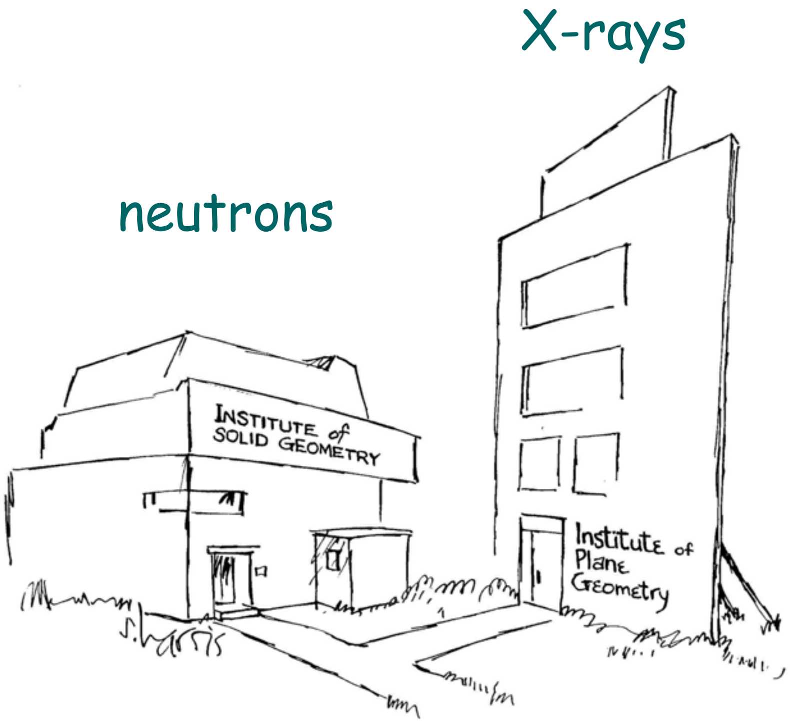
Aim for time resolution from milliseconds to a few minutes, i.e. faster what can be done on high-resolution neutron diffractometers

Follow details of phase transformations and chemical reactions to better understand the underlying mechanisms

Message 1 Working in new time domains open one's eyes to phenomena un-seen and even un-thought off

Corollary to 1 There is room for improvement in detectors

Why neutrons ?



Time-resolved studies are almost never at ambient conditions ⇒ Complex sample environment (p,T,x): Neutrons perform well

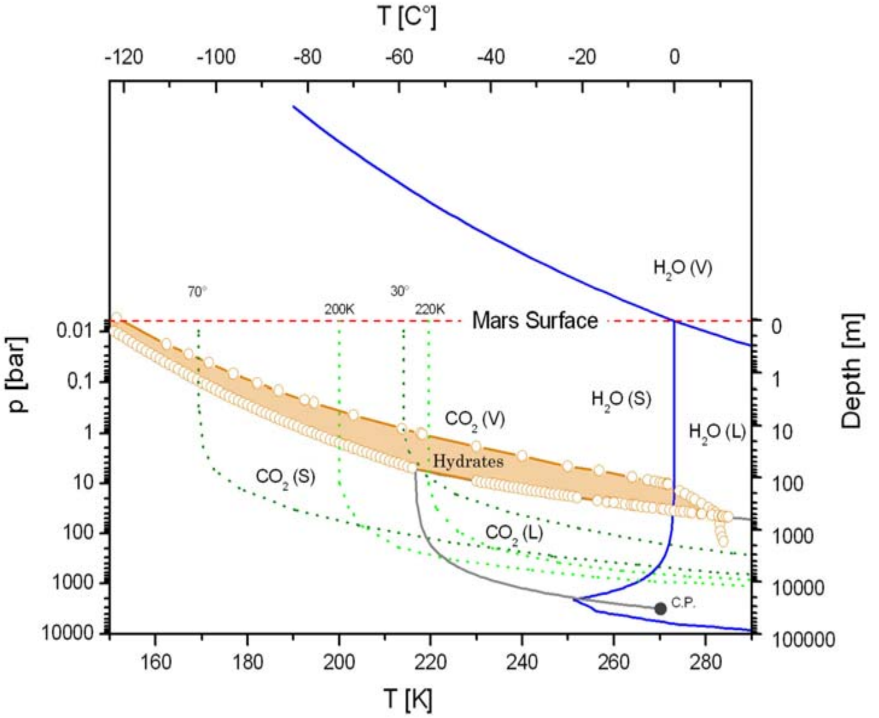
Reaction and transformation kinetics are usually bulk phenomena ⇒ Need bulk samples: Neutrons hard to beat

The reactions often go irreversably ⇒ Need a stable source: (reactor) neutrons offer this

Message **2** Neutrons are really very good friends of real time studies

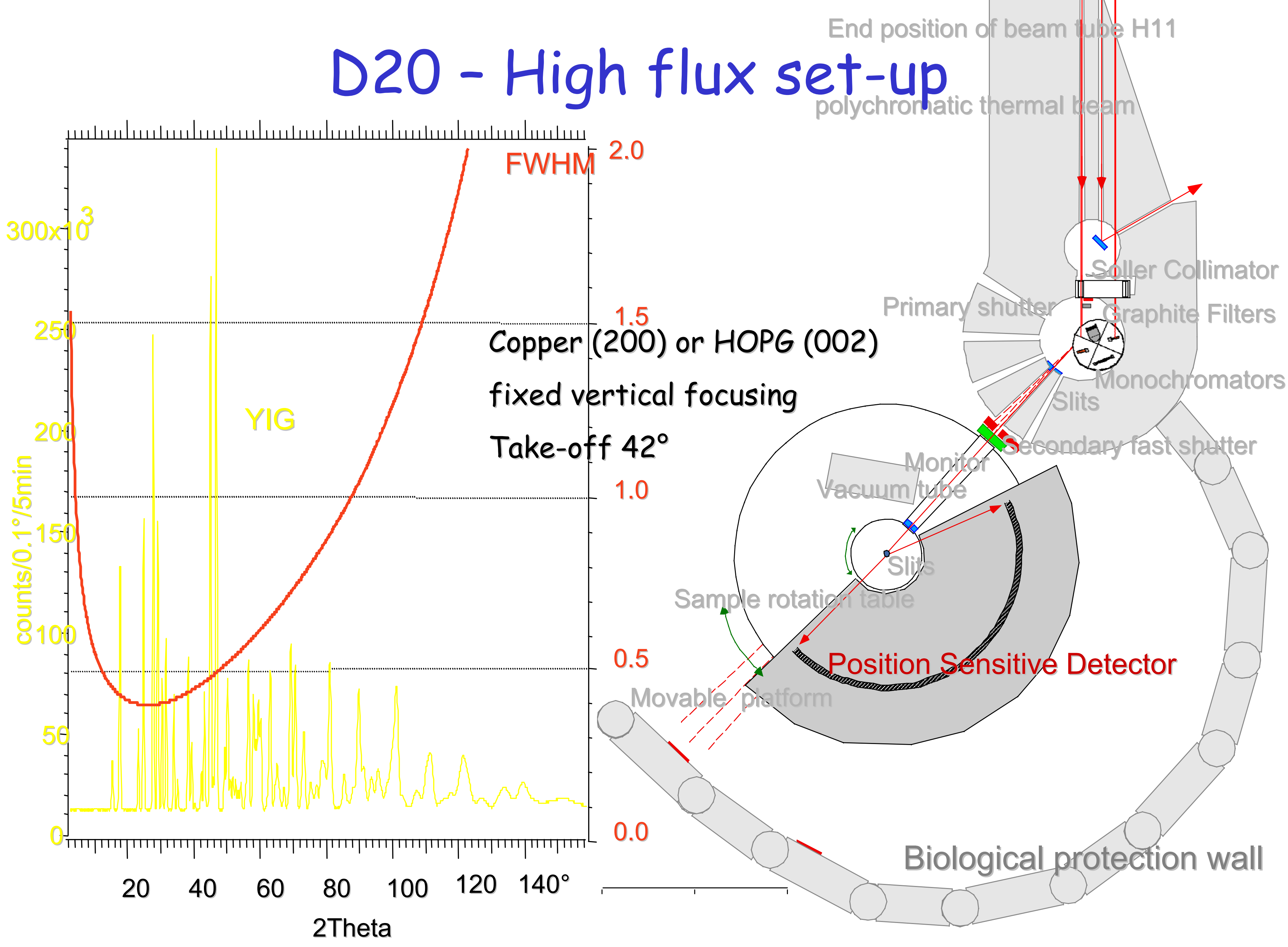
Natural processes are usually slower …

Example: Can CO_2 hydrates be formed on the Mars surface in Martian winter ?



Message **3** Establish a model for the reaction/ transformation kinetics and then extrapolate

D20 - High flux set-up

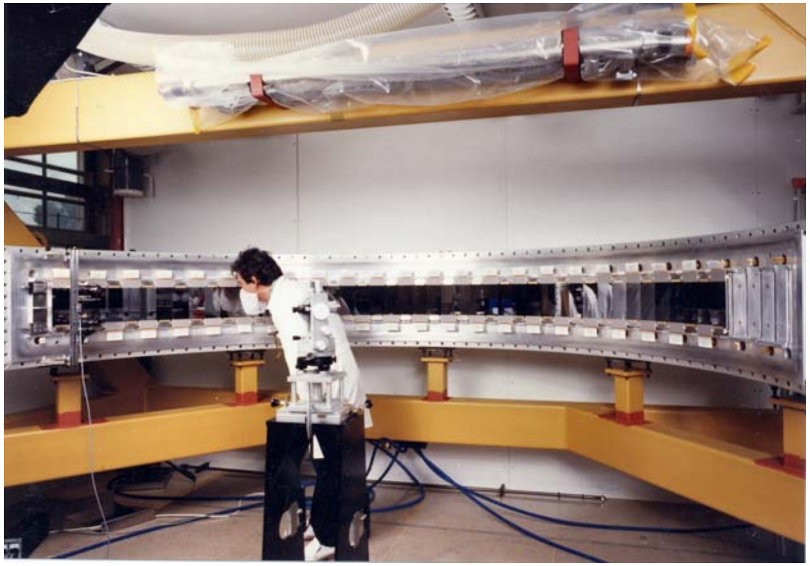


Copper (200) or HOPG (002)

fixed vertical focusing

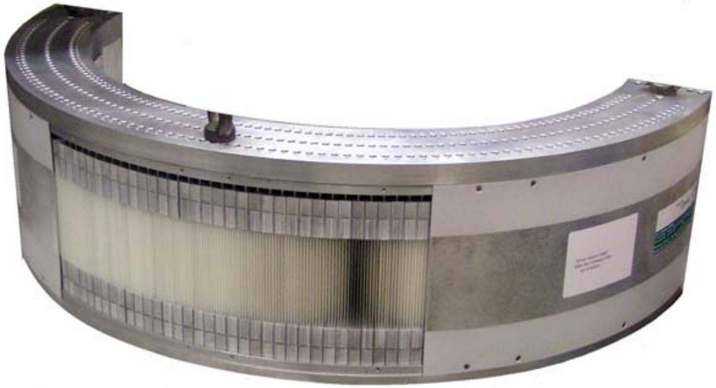
Take-off 42°

See it all at once: large detectors



…and store it fast

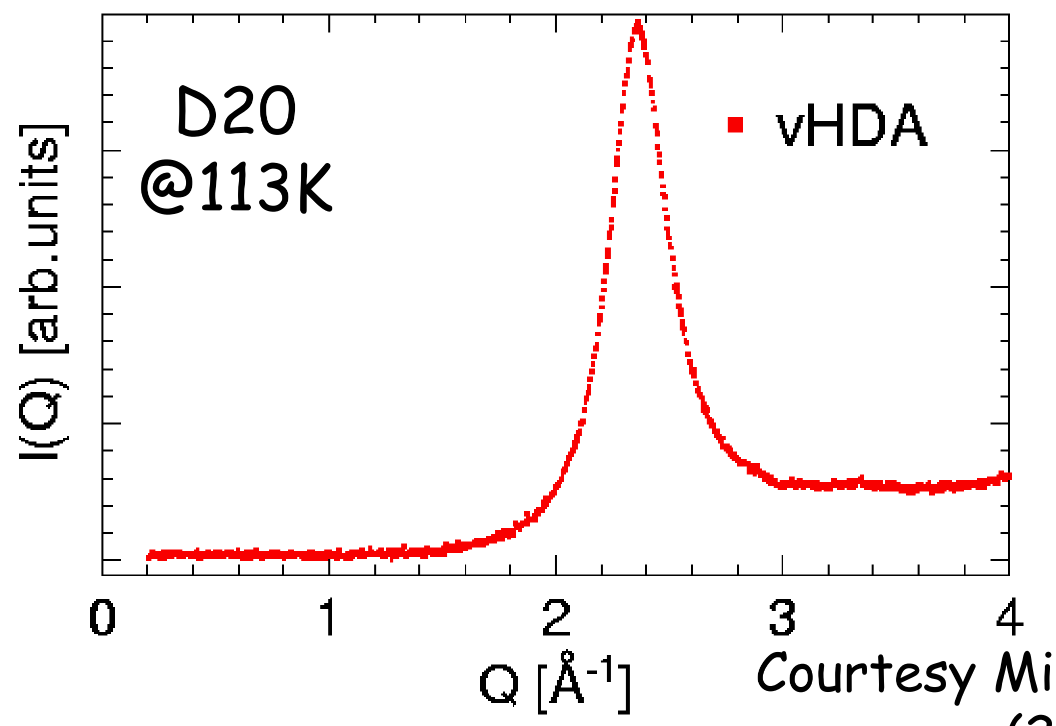
D20 microstrip multi-detector with 153.6° coverage in 2Θ and a definition of 0.1°.



D20 radially oscillating collimator (ROC)

…but **only** see the sample: large ROCs

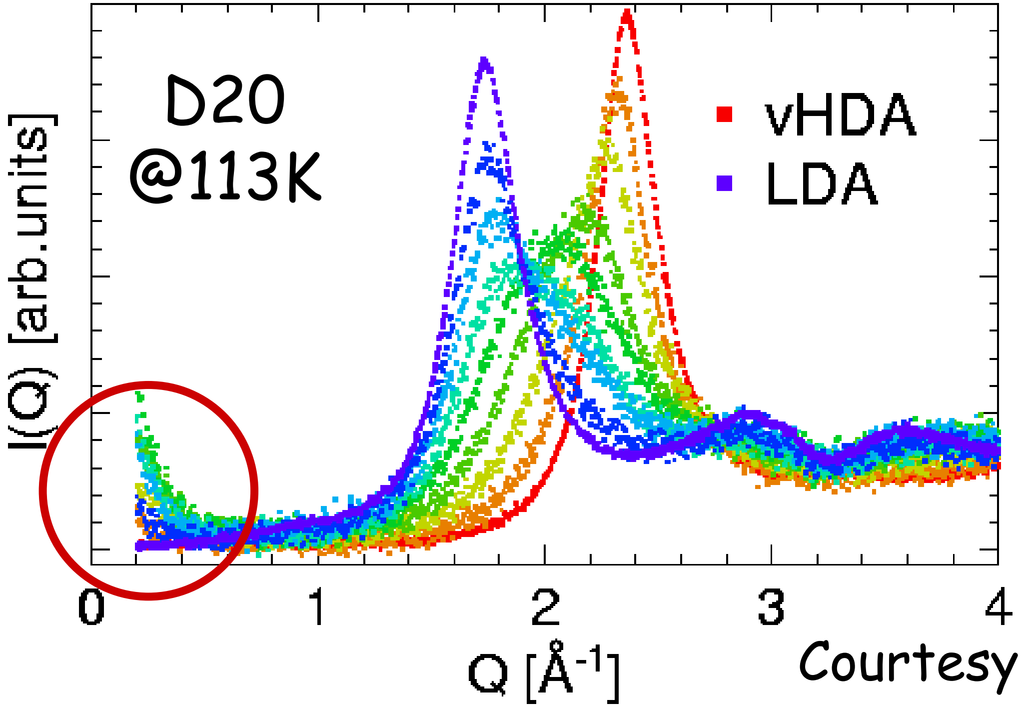
In situ observation of structure changes going from vHDA to LDA ice



Courtesy Michael Koza PRL (2005)

NB: The character of the phase transition between HDA and LDA is important for understanding the much discussed second critical point of water.

In situ observation of structure changes going from vHDA to LDA ice



Courtesy Michael Koza

Continuous structural changes, however, with a transient heterogeneous character as seen in the small angle scattering.

Message 4 Large detectors see the unexpected

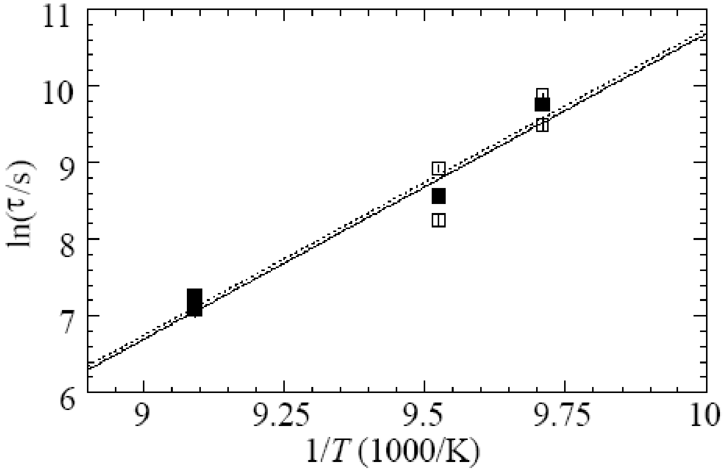
Kinetics of HDA to LDA water transition

1. In situ sampling of structure factor

2. Measure at different temperatures
   Fit to Avrami-Kolmogorov equation
   $I(t,T) = (1 - C) + C \cdot \exp[-(t/\tau(T))n] + B \cdot \ln(t)$

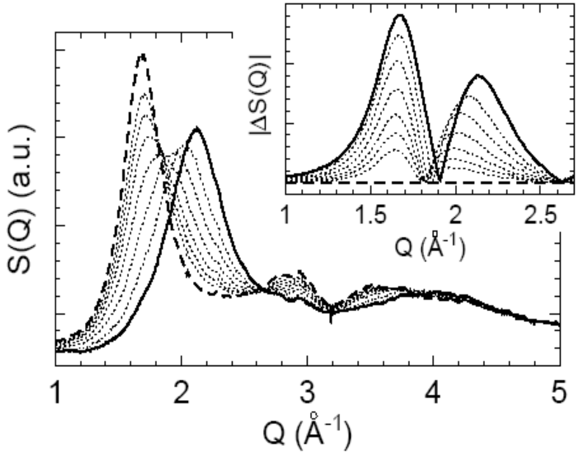
3. Phase fraction changes yield a time constant τ for each temperature
   Arrhenius eq.: $\tau(T) = \tau\infty \cdot \exp(\Delta E/RT)$
   -> **Activation energy**

3.

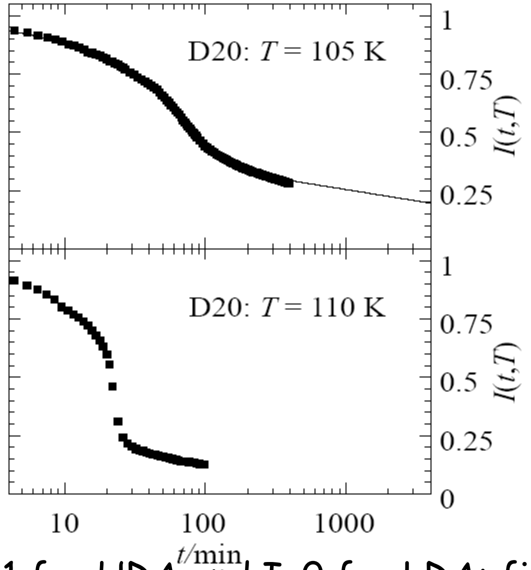


Arrhenius plot yields 33± 2 kJ/mole

1.



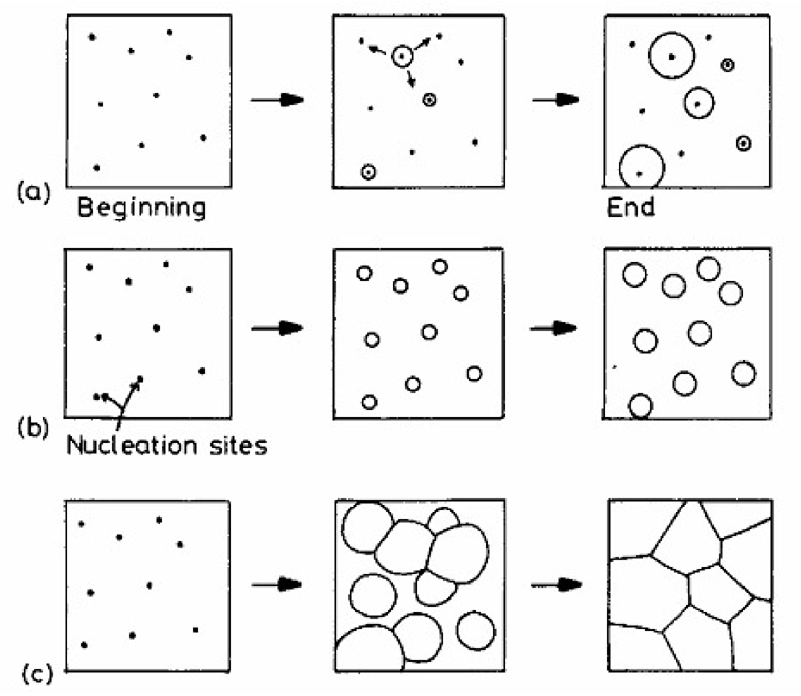
2.



I = 1 for HDA and I=0 for LDA; fit is a superposition of HDA annealing (logarithmic) and a sigmoidal AKE

Johnson-Mehl-Avrami-Kolmogorov

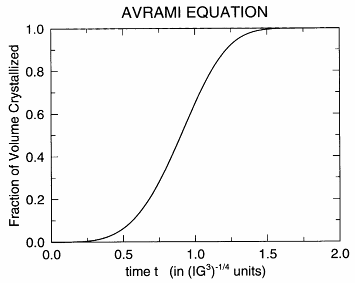
Assumption: Nuclei are randomly distributed in space



Continuous nucleation:
nuclei added
during transformation.

Site Saturated:
all nuclei present
at $t=0$.

Cellular:
e.g. recrystallization;
kinetics same as for
site saturated case.



The transformation kinetics are universal. They are described by a S-curve; slow at first, then accelerating, then decelerating.

The Avrami equation

$$f \quad = \quad 1 - \exp - \left\{ kt^{n} \right\}$$

f is the fraction transformed. The value of the exponent n relates to the dimensionality of the growth:

Site saturated:

1D growth	1
2D growth	2
3D growth	3

Continuous nucleation with constant nucleation rate:

1D growth	2
2D growth	3
3D growth	4

GEO (CHE, MSCI) meet neutron physics

"I'm on the verge of a major breakthrough, but I'm also at that point where chemistry leaves off and physics begins, so I'll have to drop the whole thing."

What is measured? Intensity changes or phase fractions usually obtained from Rietveld techniques

What to do with the data? Compare them with rate equations from

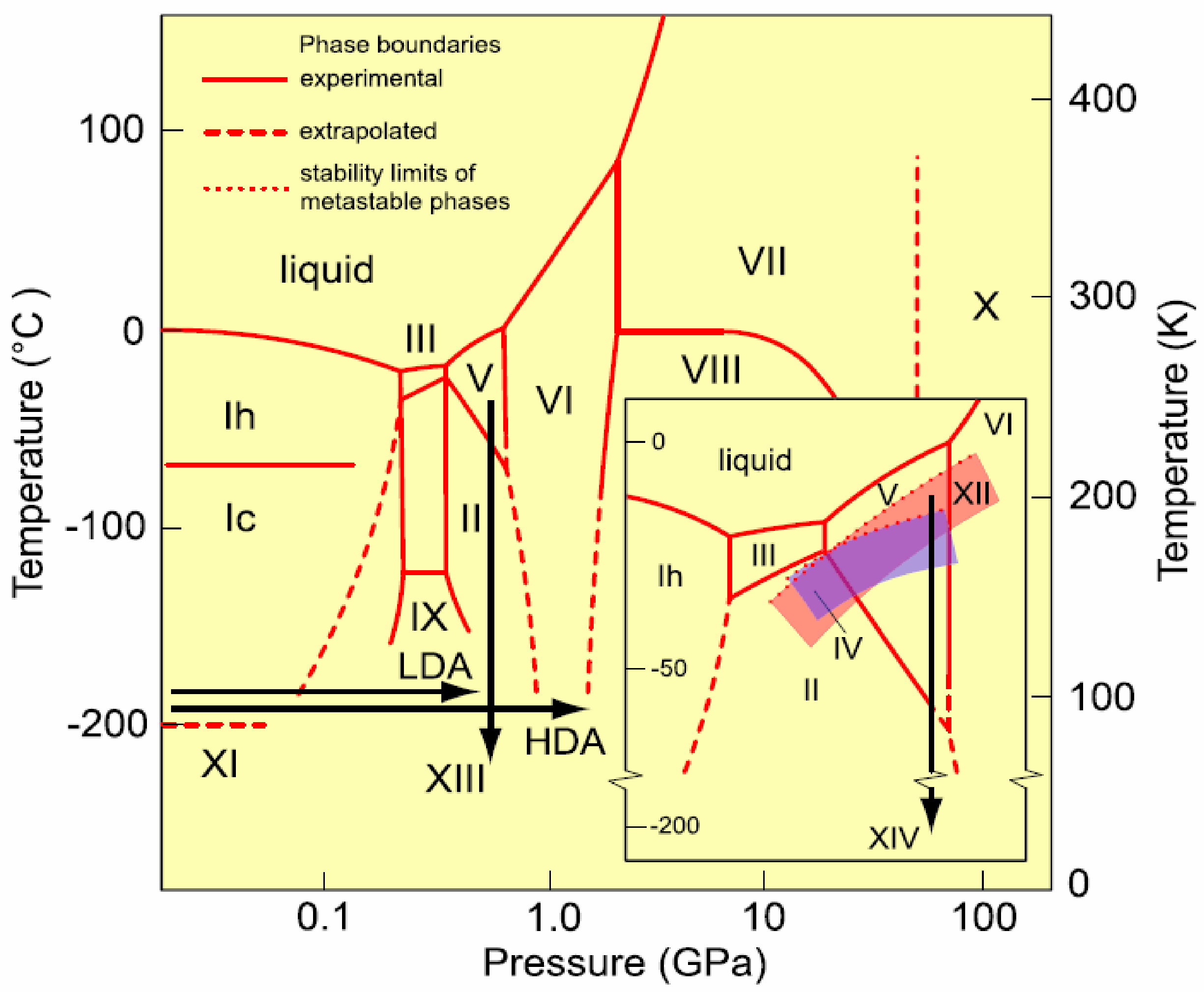
Avrami models (nucleation/growth limited) or

shrinking core models (diffusion/ reaction limited) or .....

What is obtained? Insight into rate limiting elementary processes, their activation energies etc.

Message **5** Crossing borders to other disciplines is quite revealing – scientifically and socially
Corollary to 5: This is an activated process !

Phase diagram of water



Stable and metastable phases

Two types of phase transitions:

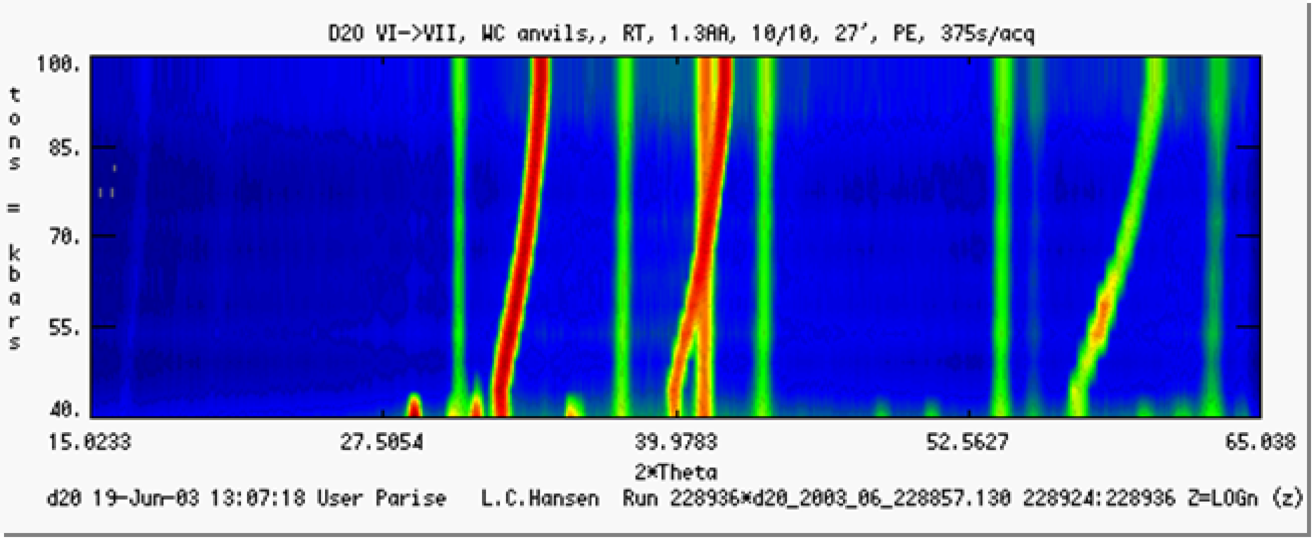
Topological and proton (dis)ordering

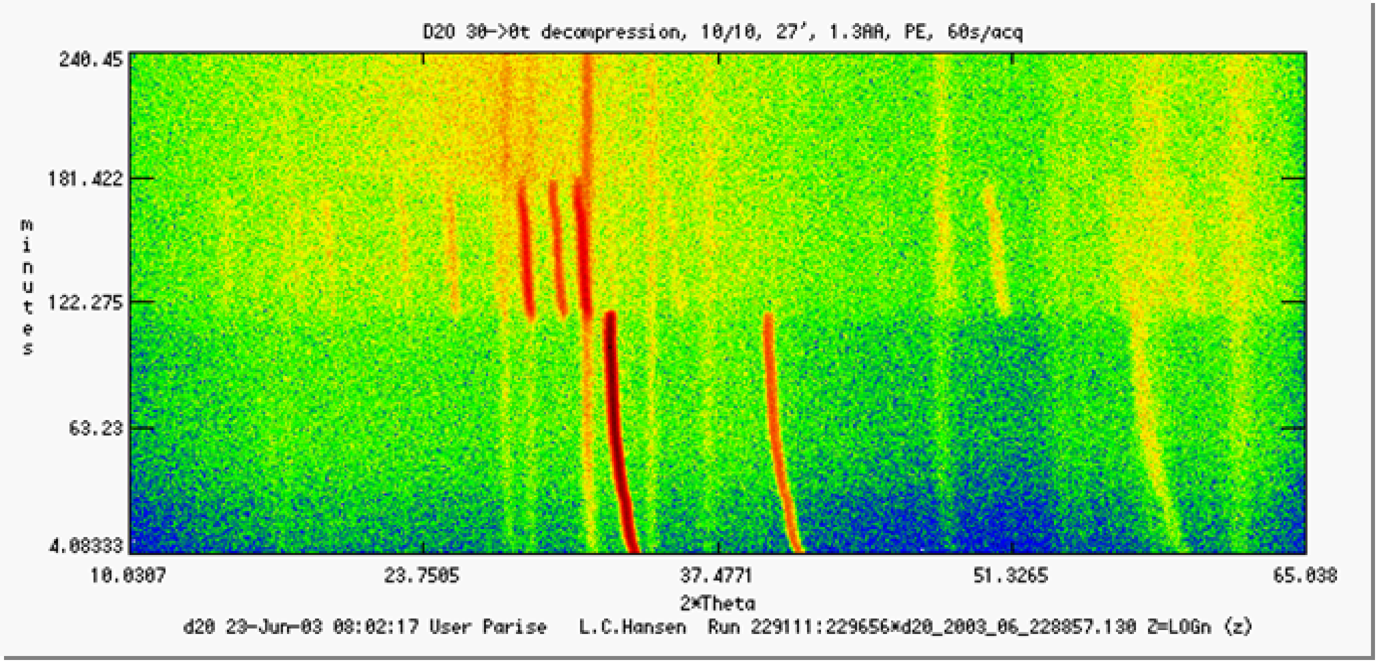
Not much known about the transition kinetics …

A widely open field to learn more about H-bonding in water systems.

Transitions between HP ices

- Test experiment on D20 with PE-cell (John Parise et al.)
- Ice VI-VII phase transition on compression

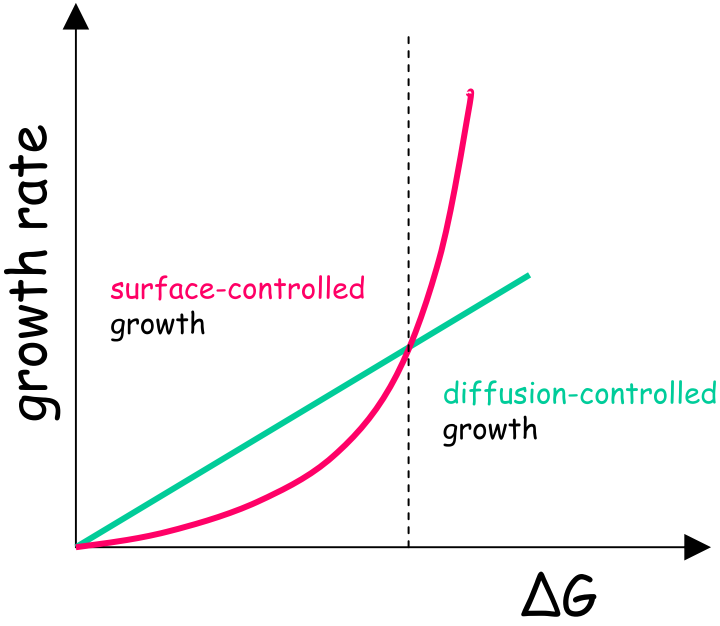




- Decompression VII -> VI -> liquid 60s per diagram

NB: Driving force (over- or under-pressure) kept changing !

The thermodynamic driving force



Surface-controlled growth rate usually non-linear

Diffusion-controlled growth rate usually linear

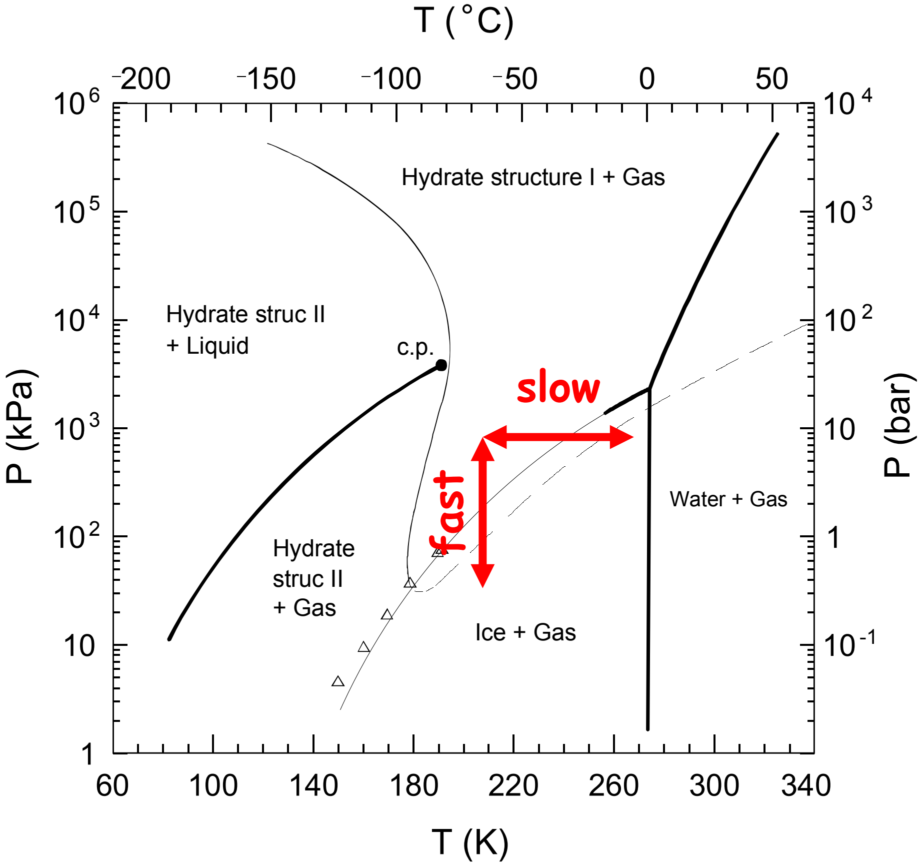
NB: This is an oversimplification

The driving force ΔG could be:

- overheating or undercooling
- over- or underpressure
- excess fugacity
- supersaturation

How to trigger a reaction ?

CH_4 - H_2O phase diagramm



External trigger (e.g. electric field, irradiation with light) can be used on reversible processes (stroboscopic measurements)

For non-reversible reactions one needs to quickly enter or leave the stability field by changing p, T or chemical activity (composition)

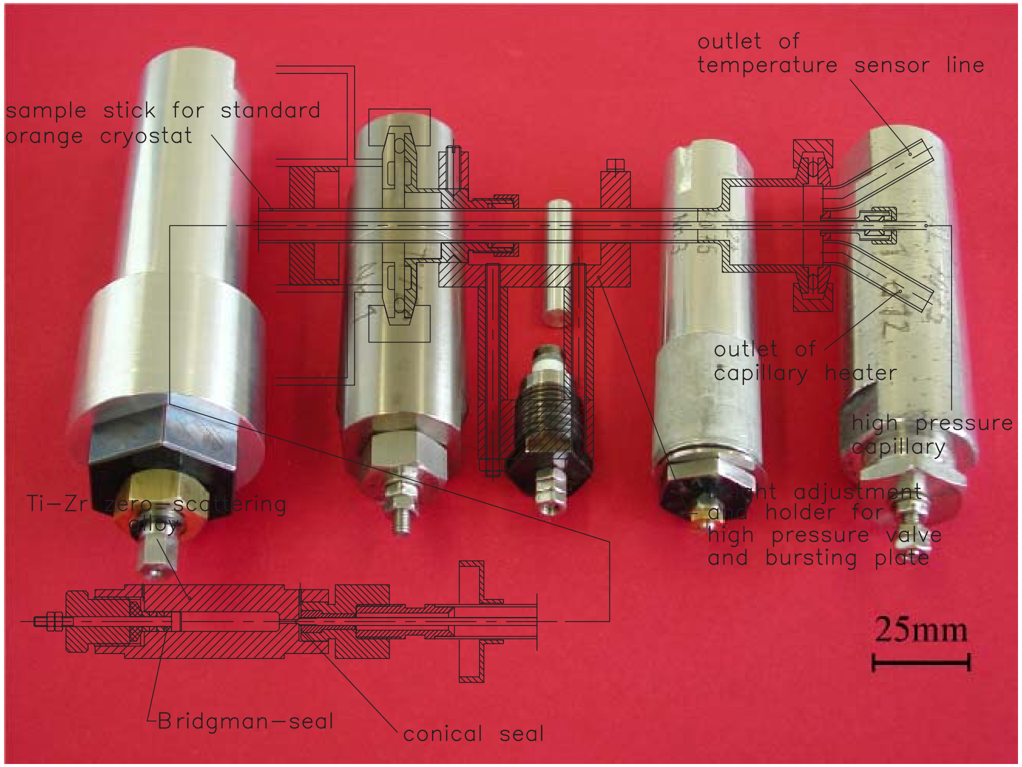
Temperature changes are usually slow and need systems with low thermal inertia. Caveat: heat of transformation!

Pressure changes could be done more quickly, in particular using gas

Message 6 Standard sample environment provided by the neutron centres are quite often not ideal.

User-build sample environment

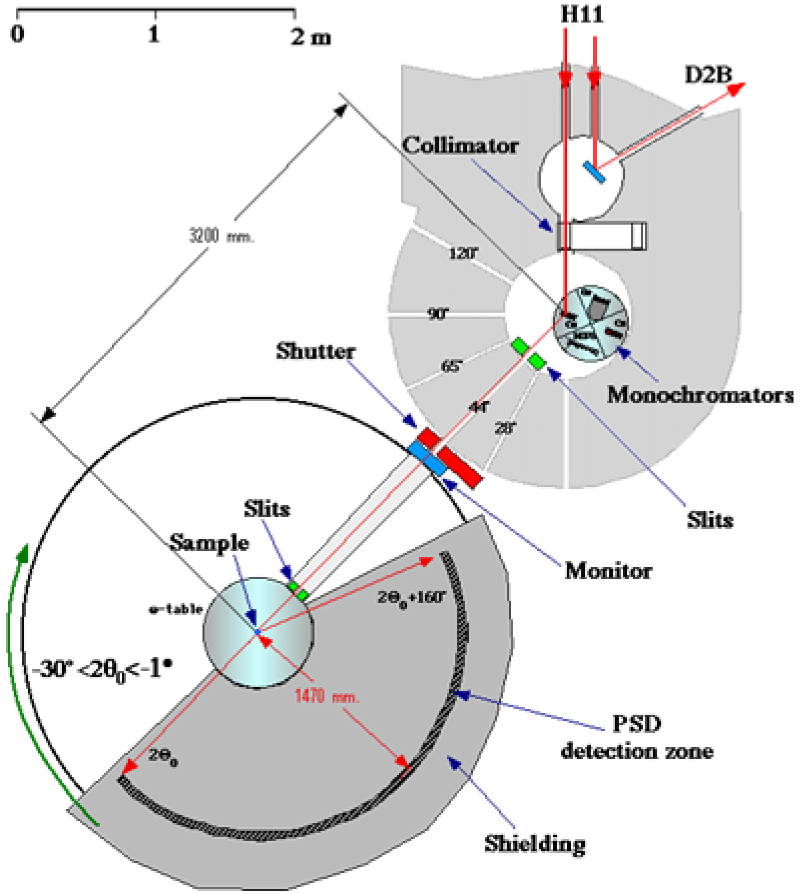
Gas pressure cells designed in Göttingen essentially for kinetic work (e.g. by optimizing the diameter to the cryostat heat exchanger)



… and closely matching the specificities of the ILL instruments, in particular D20.

Gas hydrate formation and decomposition on D20

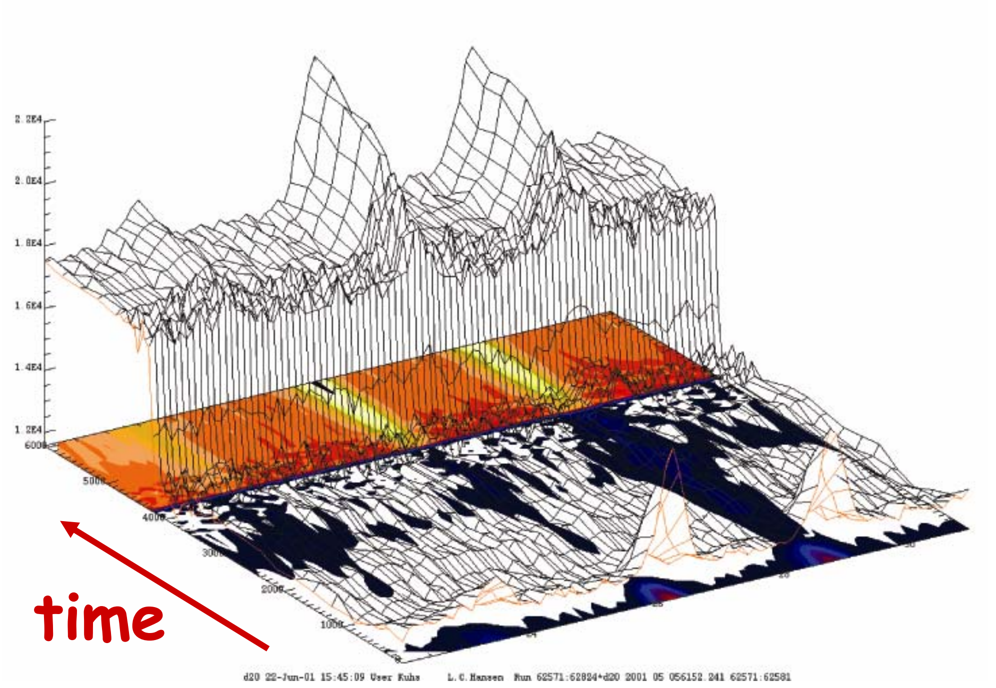
High-flux set-up on D20



Formation of methane hydrate

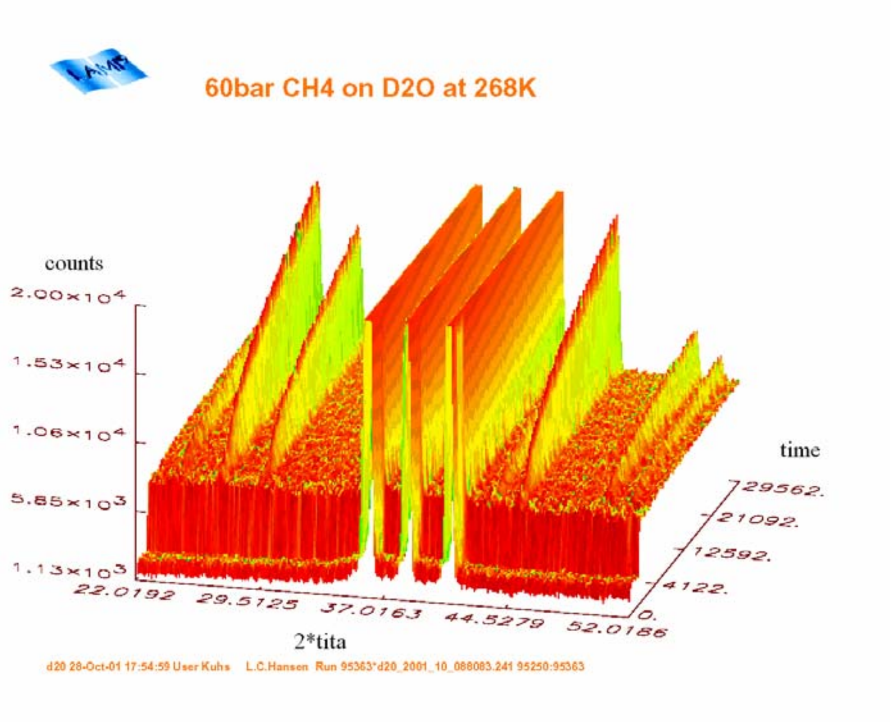
The initial phase of a reaction is usually very fast and then slows down.

Full powder pattern every 10 seconds

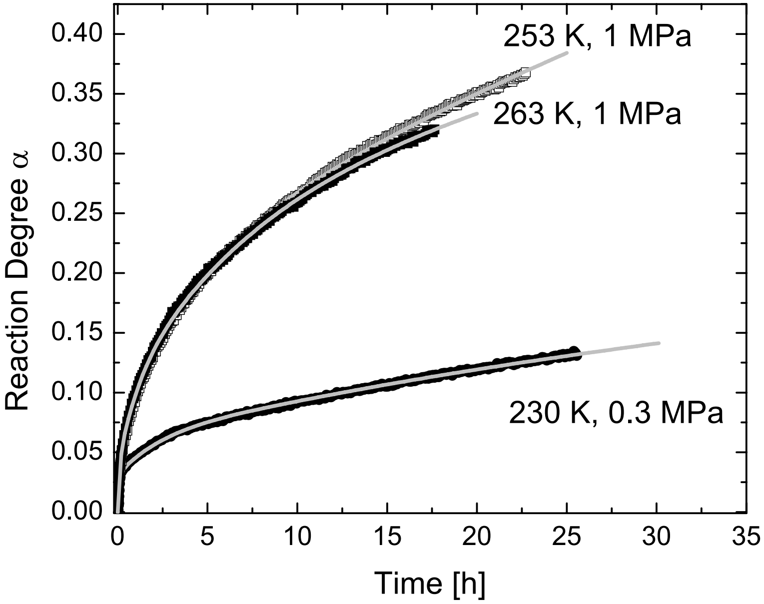


Gas hydrate formation kinetics

raw diffraction data



after "Rietvelding"



There is an excellent agreement between our shrinking core model and the experiment data (which have a precision of better than 1‰).

Modified shrinking core model

Salamatin & Kuhs (2002), Staykova et al. J. Phys. Chem. B 107 (2003) 10299, Genov et al. Am.Miner. 89 (2004) 1228, Kuhs et al. J.Phys.Chem. B 110 (2006) 13283

$-e^{-\omega_S t})]$

Surface coati

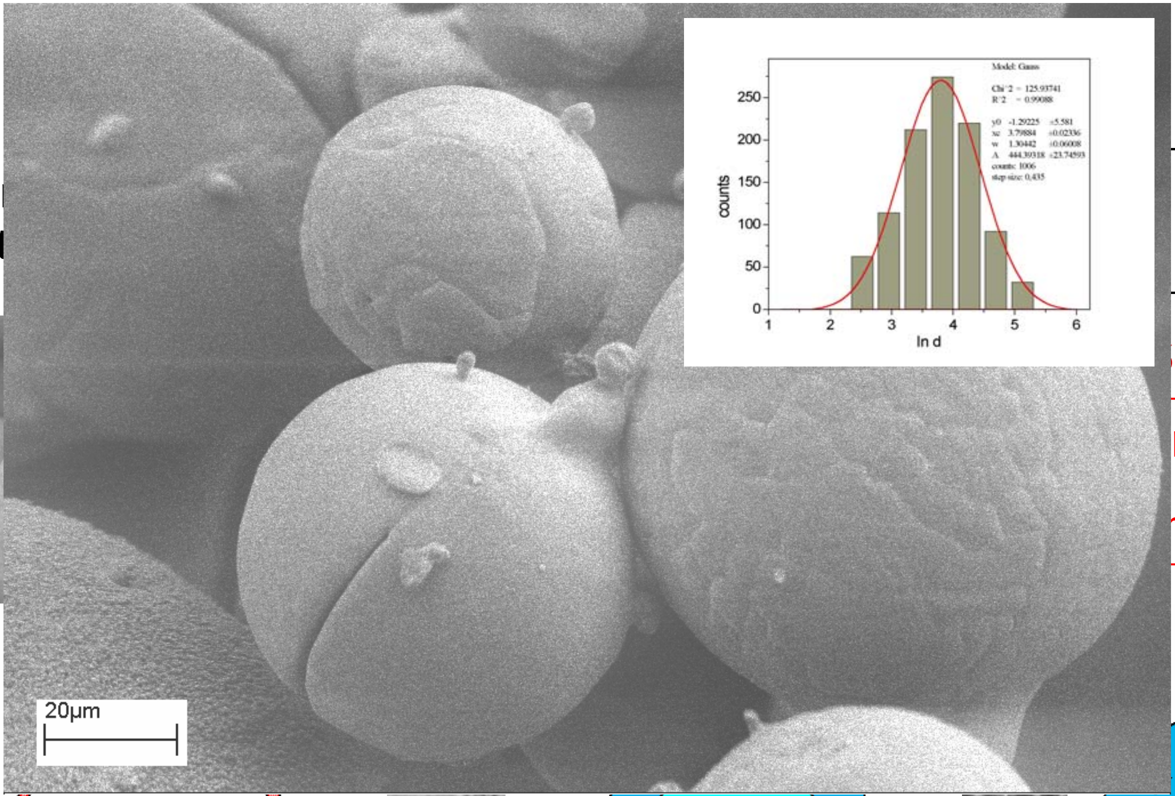
volume growt

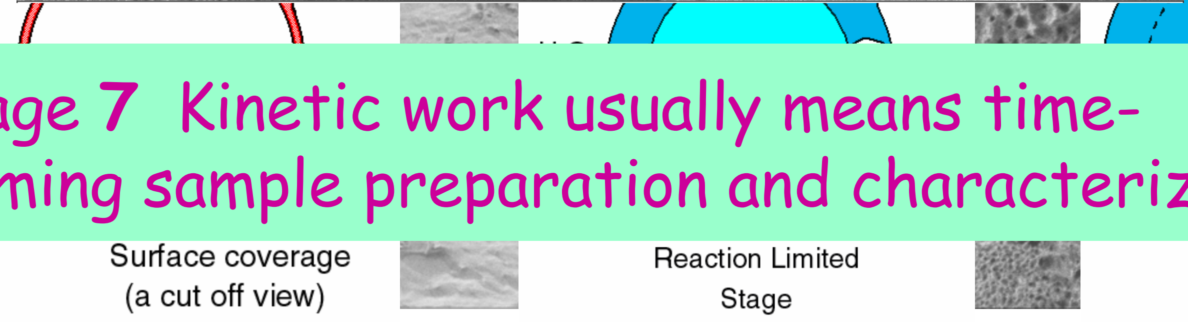
$\frac{E_i}{R_g}\left(\frac{1}{T_*}-\frac{1}{T}\right)]$

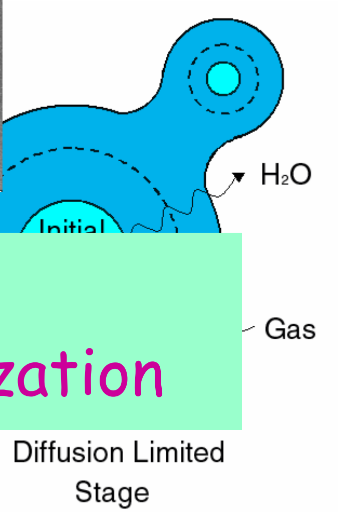
- behaviour

rate (for same f/f$_d$)

n 32 to 55 kJ/mol



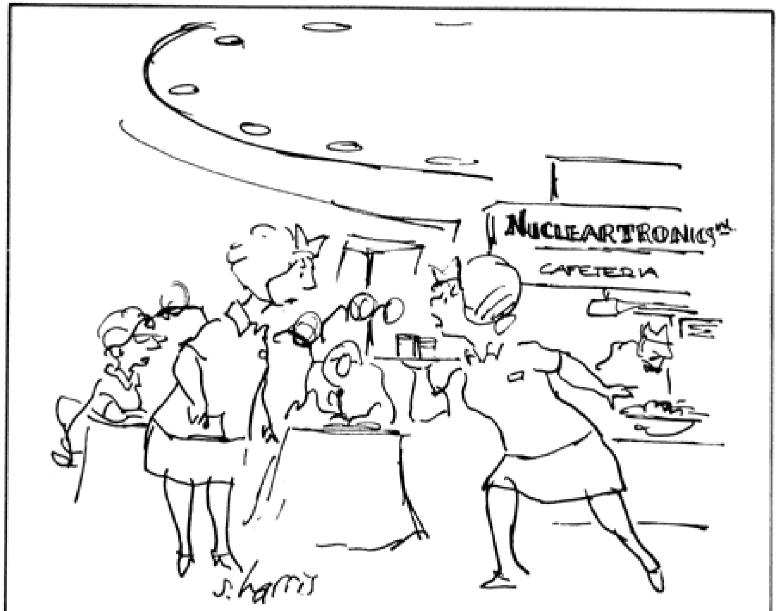




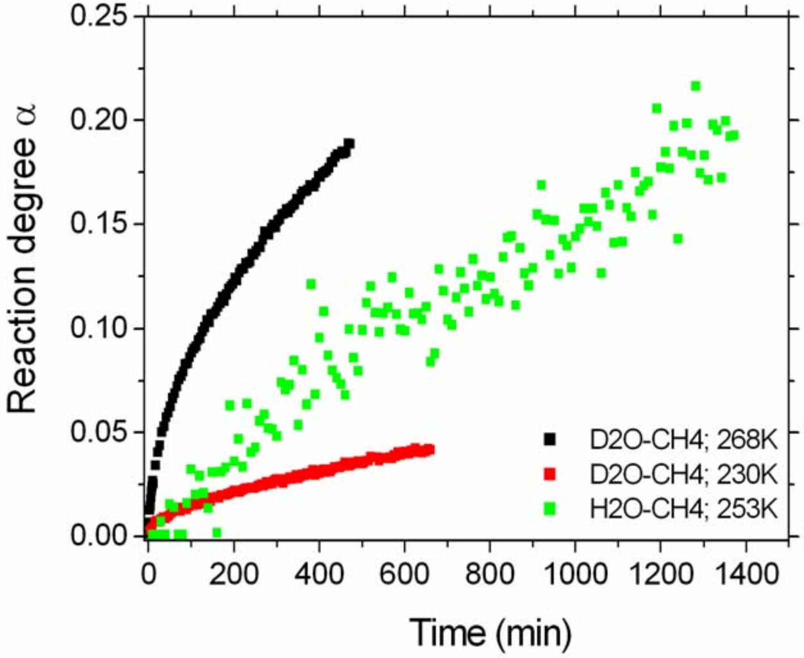
Message 7 Kinetic work usually means time-consuming sample preparation and characterization

H versus D

Systems in real life are not deuterated



"You know what I hate about this place? The heavy water."

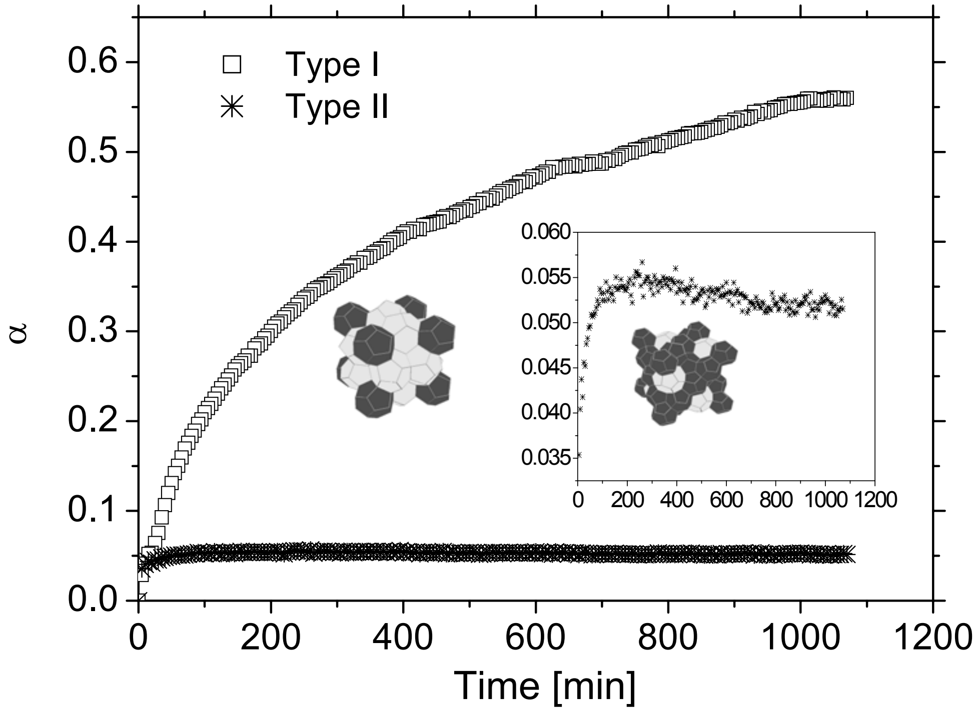


Use **annular sample containers** to avoid absorption problems, see Schmitt and Ouladdiaf (1998)

Message **8** Deuteration is not always mandatory !
Corollary to **8** A factor of 10 in precision would be welcome.

Existence of intermediate phases

… is often best seen by diffraction !



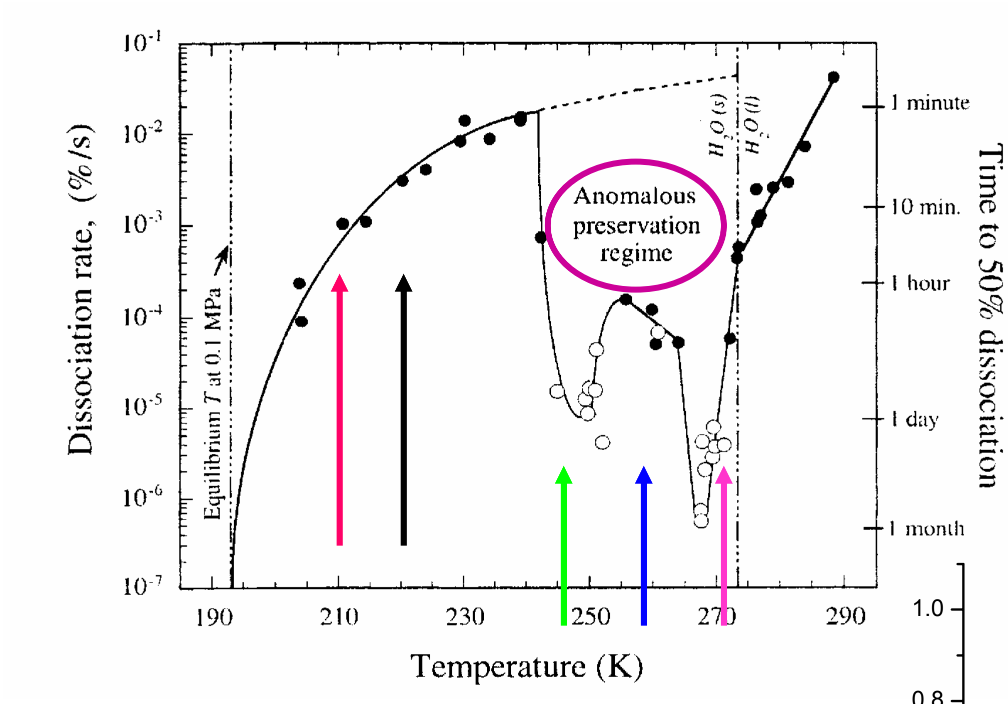
Deuterated CO_2 hydrate @ 20bar and 0°C

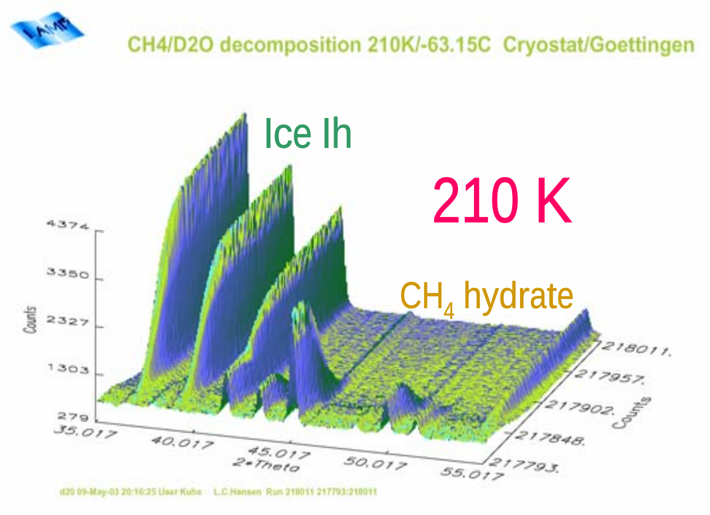
Insert shows type II fraction, which was unexpected

Message 9 Excellent counting statistics of D20

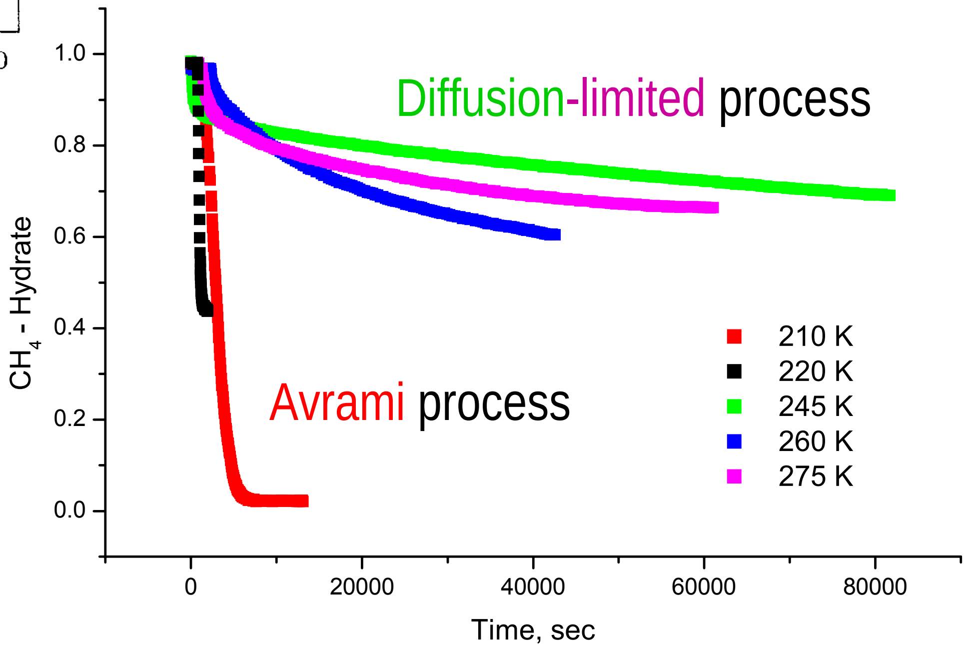
Corollary to 9 You hardly miss the unexpected !

CH_4 hydrate decomposition and anomalous preservation



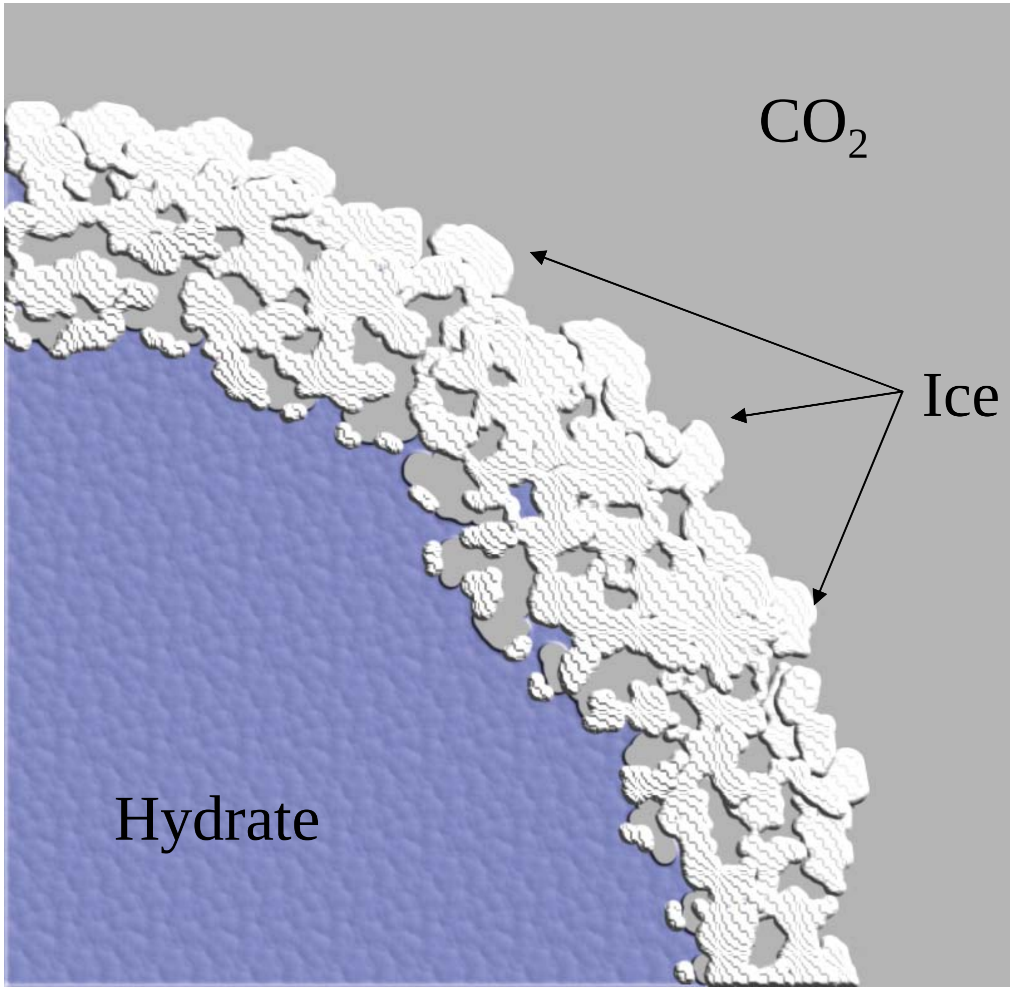


How does anomalous preservation work ?



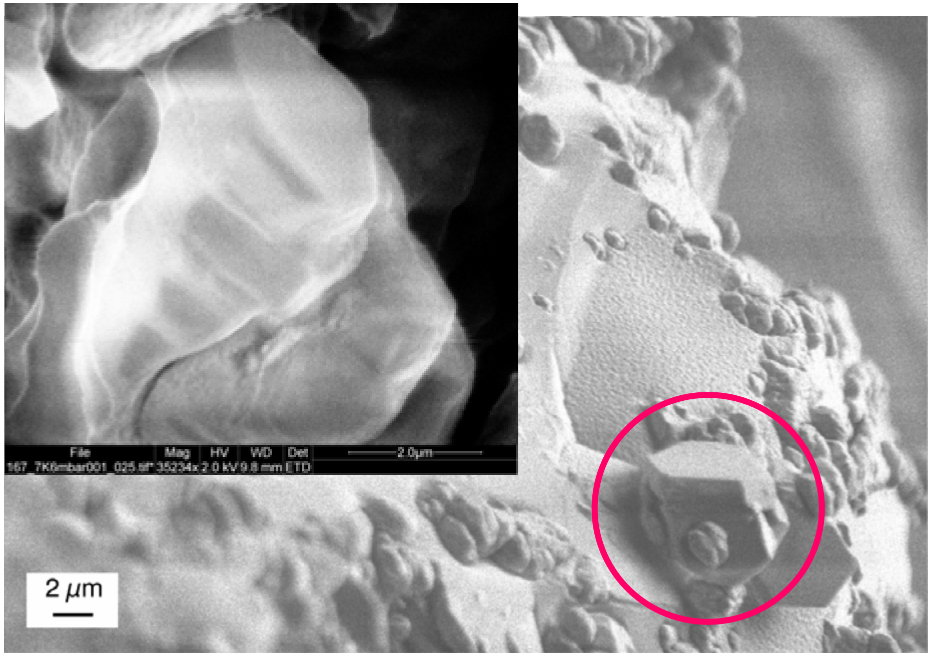
Gas hydrate decomposition pictorial

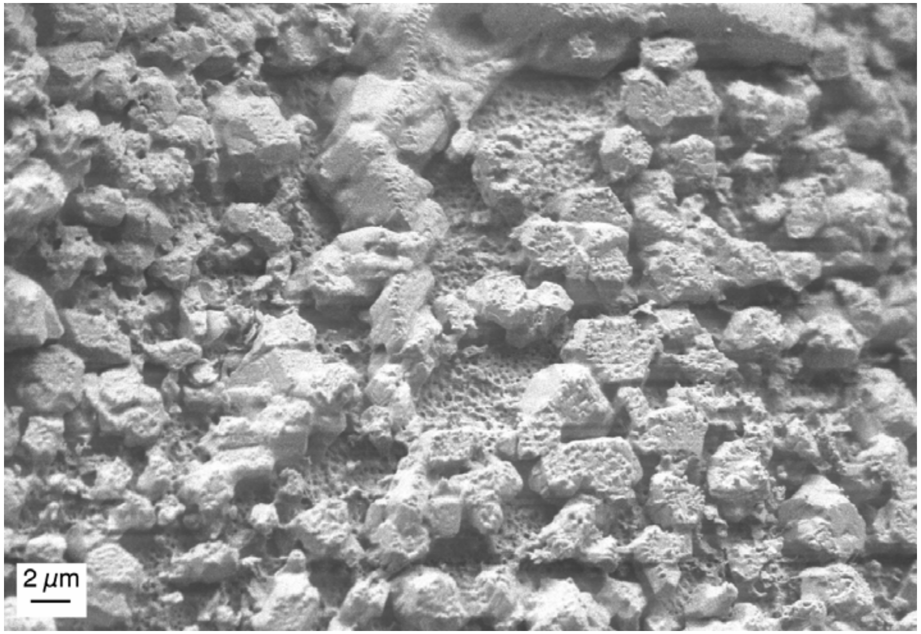
Situation below anomalous preservation T-range



Ice nucleation on gas hydrate surface

Interrupted decomposition runs studied (ex-situ) by cryo-SEM



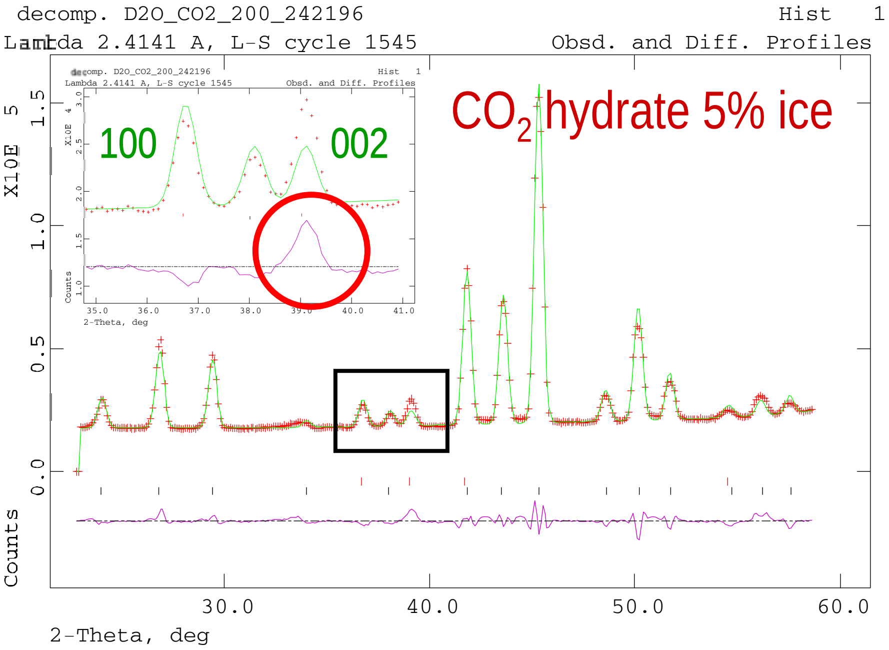


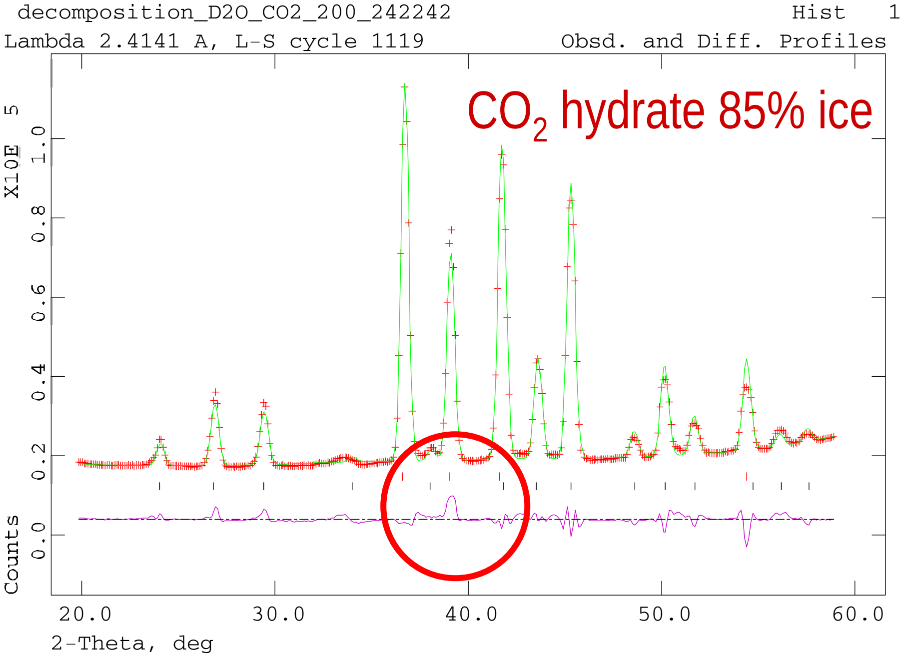
Many nucleation sites (approximately 10^5-10^6 mm^{-2})

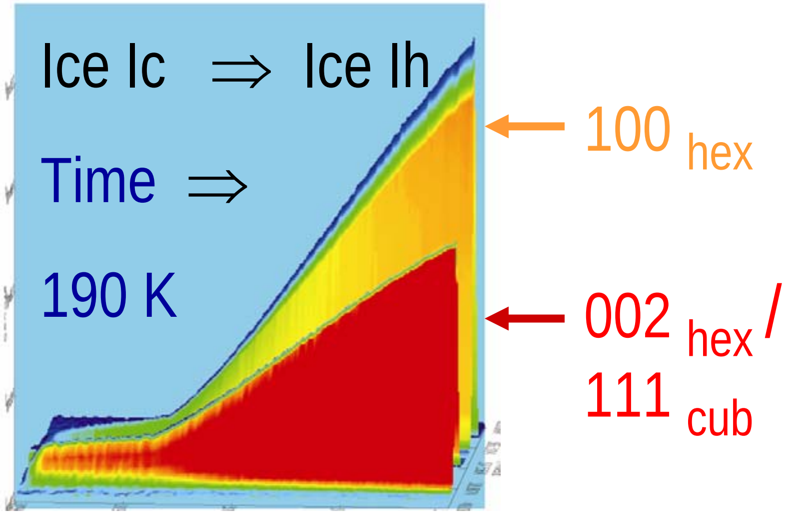
Topotactic relationship between gas hydrate substrate and ice

Message 10 Combine neutrons with other techniques !

Time dependence of ice perfection



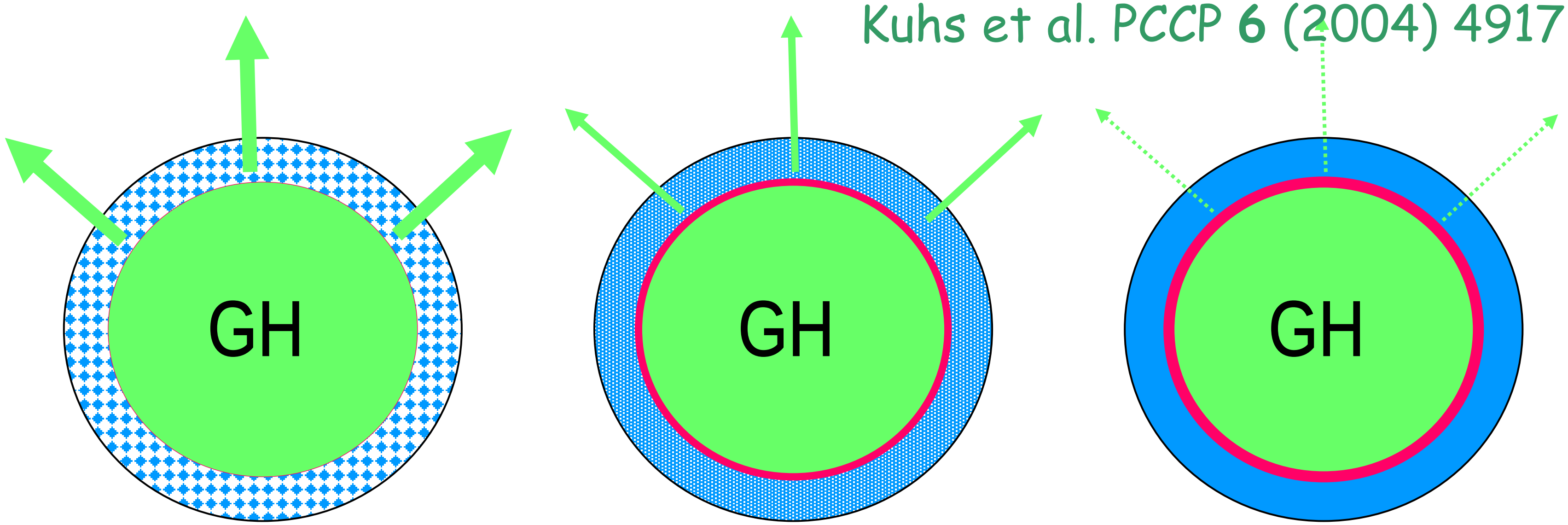




There is some annealing of the ice formed, but appreciable stacking fault defects remain at T < 240 K.

Anomalous preservation pictorial

Kuhs et al. PCCP **6** (2004) 4917



< 239 K | 240 - 265 K | > 265 K

▨ defective ice („ice Ic“)

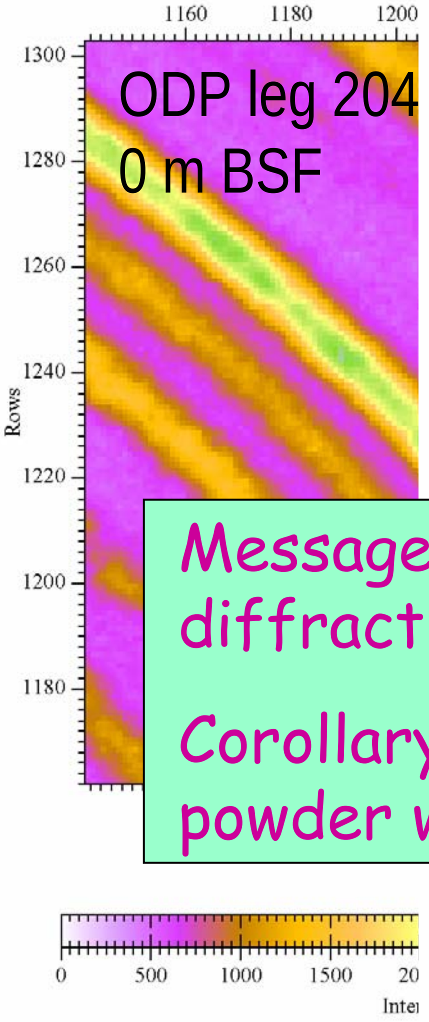
▨ ice Ih

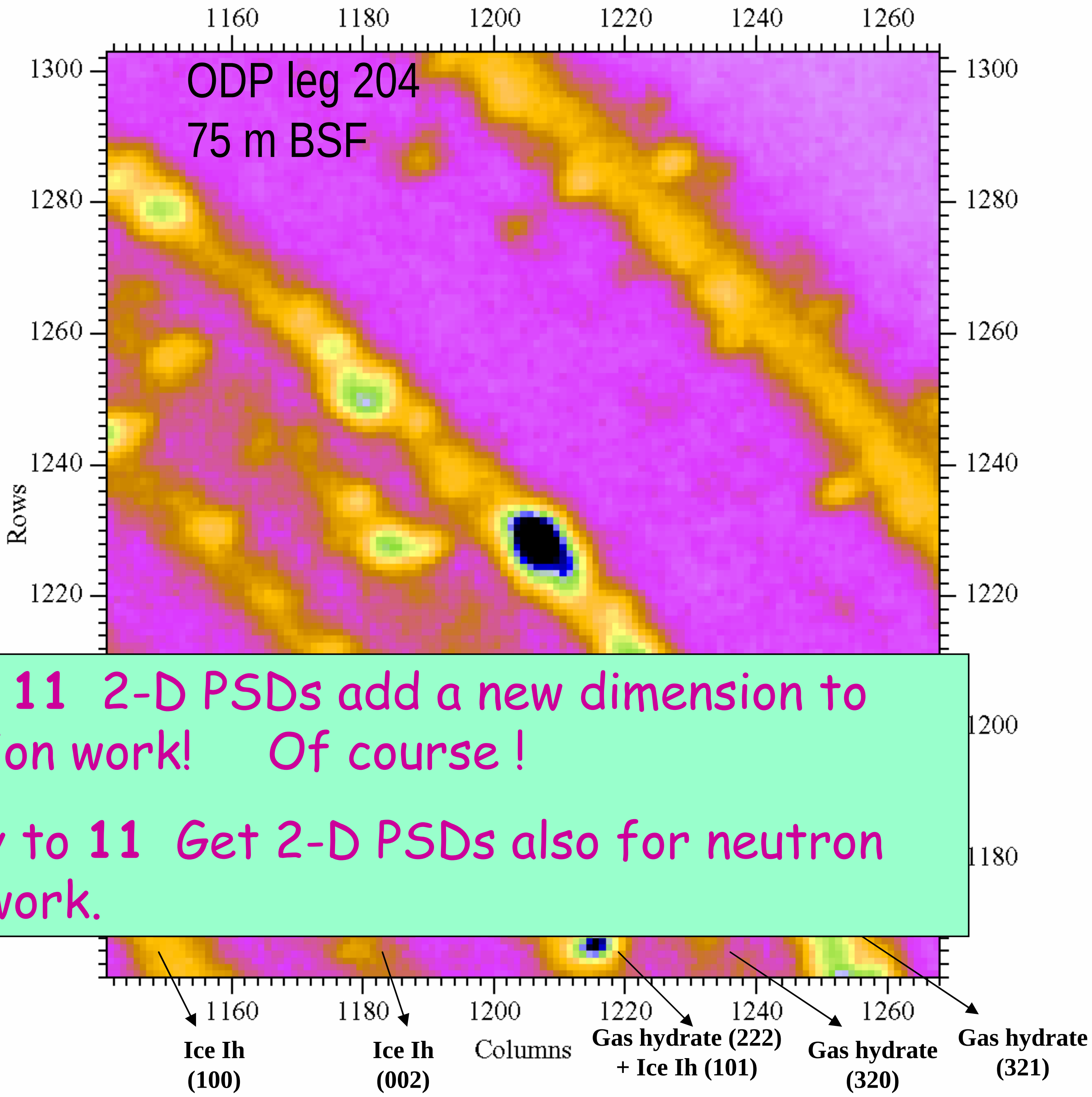
■ ripened ice Ih

All T: Decomposition reaction from gas hydrate to ice
<239K: Ice Ic (“cubic ice”) shows annealing of stacking faults
>265 K: Ice Ih shows considerable Ostwald ripening

Ice shielding effect – methane activity at interface kept high !

Natural gashydrate





Message **11** 2-D PSDs add a new dimension to diffraction work! Of course !

Corollary to **11** Get 2-D PSDs also for neutron powder work.

DRACULA @ ILL

Alan Hewat & Henry Fischer

Will provide very high flux and operates with a 2D detector

	D20	GEM	DRACULA	PowGen3
time averaged sample flux	5×10^7	$\sim2\times10^6$	$\sim10^8$	$\sim2.5\times10^7$
detector solid angle (sr)	0.27	4.0	1.5	3.0
efficiency	1.7	1	18	9

DRACULA 2D- detector: angular range 155° in 2Θ, vertical opening 26°, total opening 1.2 sr, radius 765 mm, definition 2.5mm

^{3}He operated at 10bar (9bar ^{3}He, 1bar CF_4) deadtime 0.6 μs allows high count rates

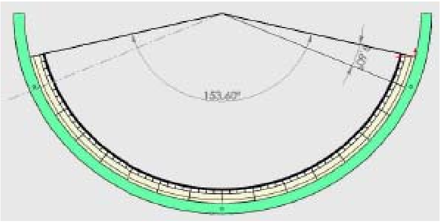
DRACULA holds quite some promise also for kinetic work

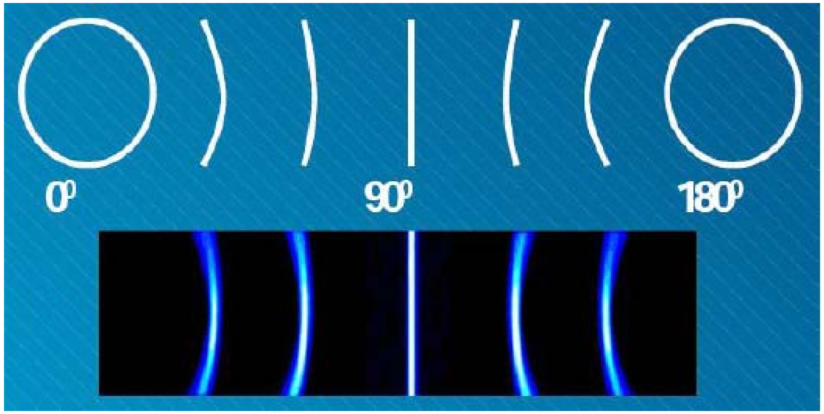
e.g. for hydrogenous samples, very small samples, extreme pressures, very fast processes …

… and try to use the full potential of 2D information !

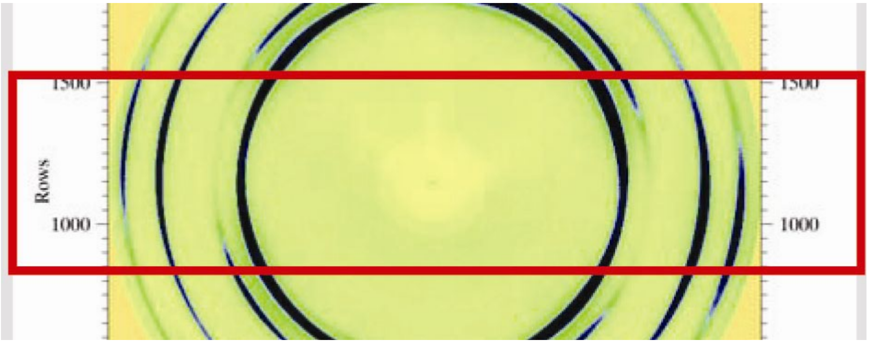
2D - Detector

for DRACULA at ILL





Debye-Scherrer cones are partly visible



Information on sample texture is directly accessible

Message **12** A 2-D detector allows for kinetic work on texture changes and recrystallization phenomena

Corollary to **12** TOF diffractometers on spallation sources have it already in principle …

Merci, Thanks, Danke !

Doroteya Staykova, Georgi Genov, Andrzej Falenty, Heiner Bartels, Eberhard Hensel, Kirsten Techmer, Alice Klapproth, @ GZG Uni Göttingen

Michael Koza, Alan Hewat, Louis Mélési @ ILL, Grenoble

BMBF and DFG for financial support

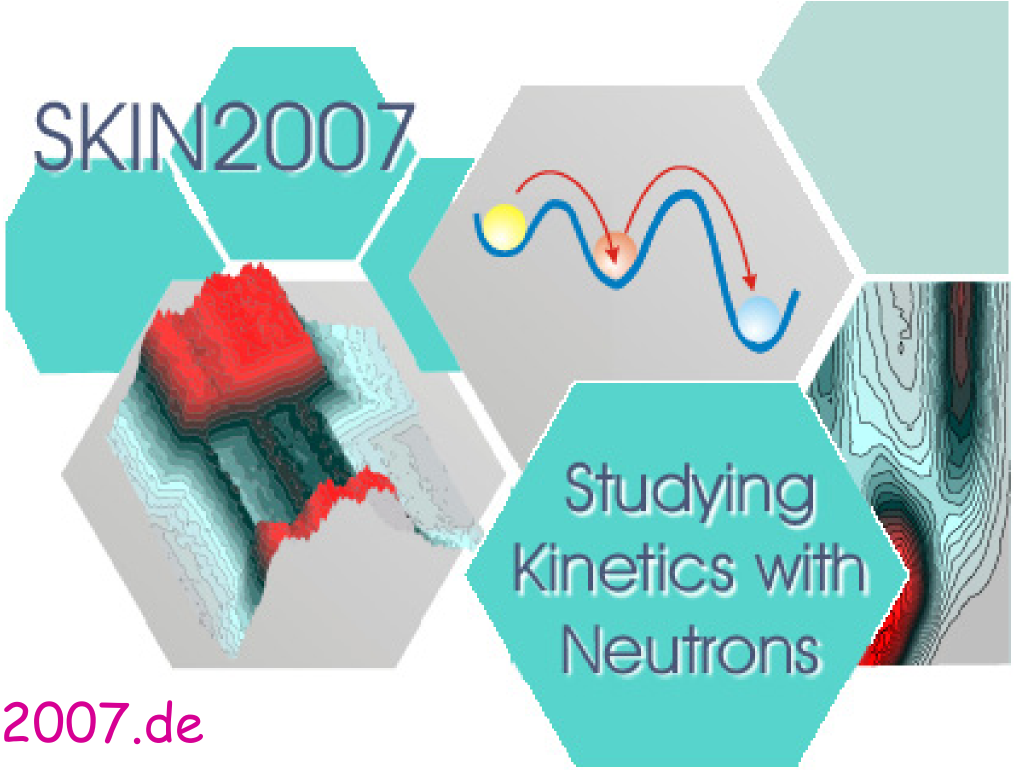
ILL/Grenoble, HASYLAB/ Hamburg for beam time and support

Deutsche
Forschungsgemeinschaft
DFG

bmb+f
Bundesministerium für Bildung und Forschung

GEOTECHNOLOGIEN

An upcoming workshop in Göttingen



http://www.skin2007.de

International Symposium on
Time-Resolved Processes in Condensed Matter

Georg-August University of Göttingen
27-28 September 2007