<u>*Euro-Conference on Rock Physics and Geomechanics*</u>

<u>*Erice, Sicily, 25-30 Sept 2007*</u>

Influence of grain boundary structure on the kinetics of pressure solution

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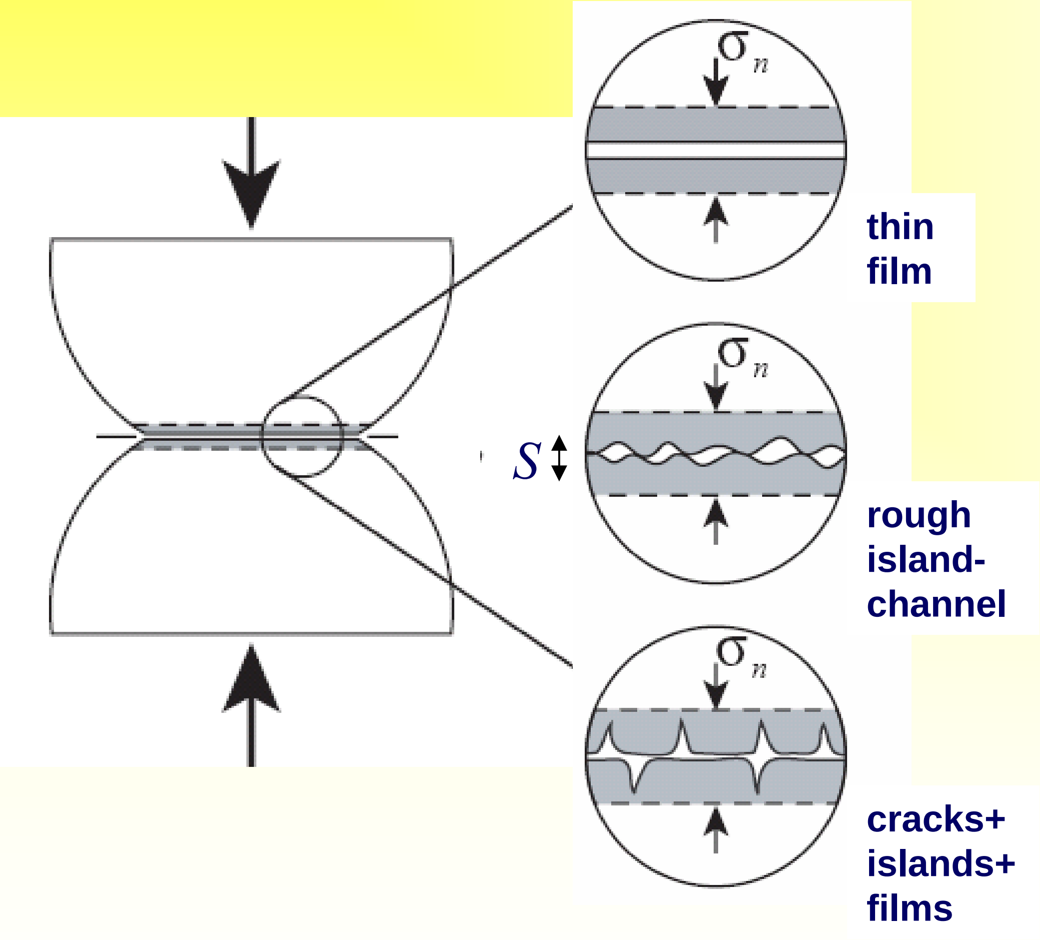
Acknowledgements to:
Siese de Meer, André Niemeijer, Rian Visser, Xiangmin Zhang

Intergranular pressure solution: ubiquitous in the wet crust

- Compaction of sedimentary rocks
- Healing, sealing and creep of faults
- Salt tectonics
- Deformation at low metamorphic grade
- Compaction of depleted reservoirs ?

So:
Much interest in quantifying IPS rates

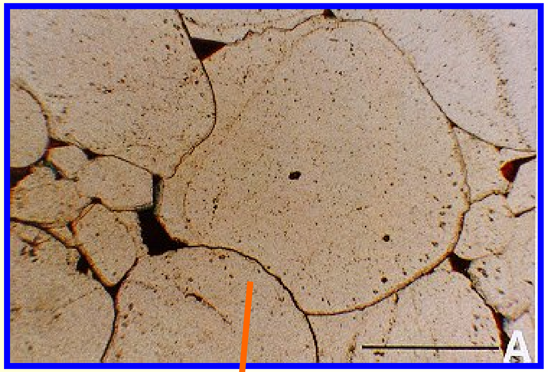
Pressure solution and grain boundary structure

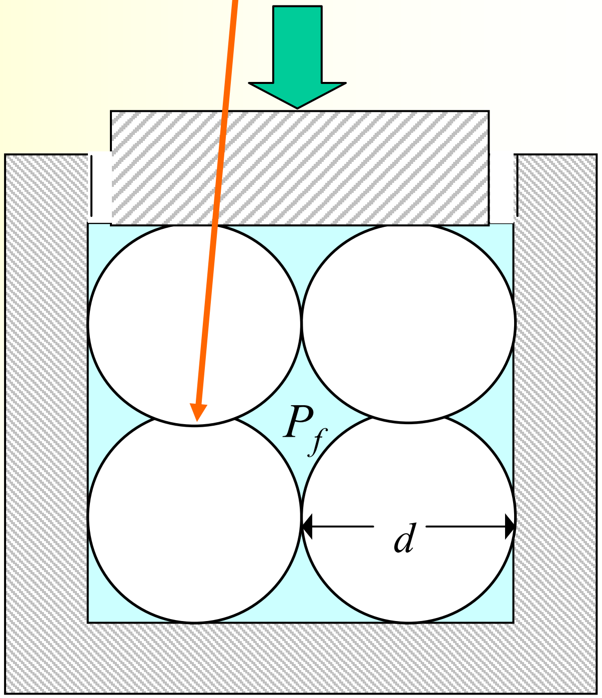


thin film

rough island-channel

cracks+ islands+ films





Theory: Compaction creep

Dissolution Control:

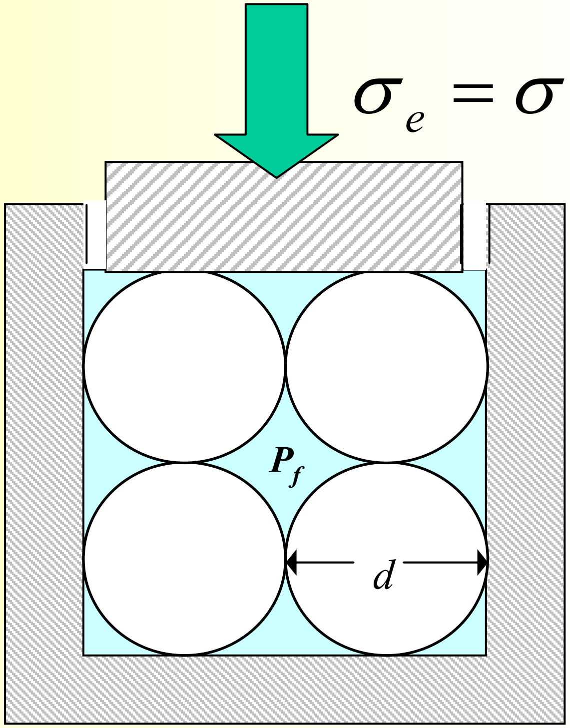
$$\dot{\varepsilon}_s = I_s \cdot \frac{\sigma_e}{d} \cdot f_s(\phi)$$

Diffusion Control:

$$\dot{\varepsilon}_d = [DCS] \cdot \frac{\sigma_e}{d^3} \cdot f_d(\phi)$$

Precipitation Control:

$$\dot{\varepsilon}_p = I_p \cdot \frac{\sigma_e}{d} \cdot f_p(\phi)$$



$$\sigma_e = \sigma - P_f$$

When σ_e is high:

$$\sigma_e \rightarrow\rightarrow \frac{1}{\Omega}\exp\left\{\frac{B\sigma_e\Omega}{RT} - 1\right\}$$

Controlling kinetic parameters

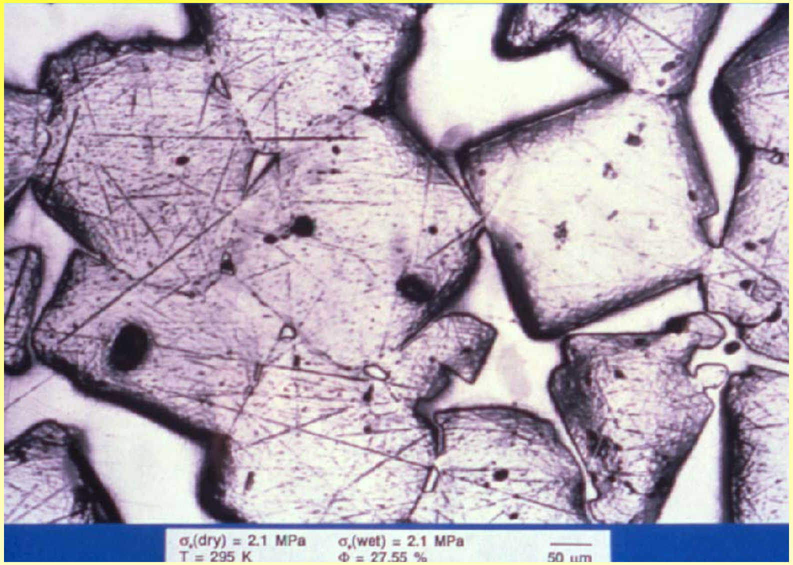
$[DCS]$, I_s and I_p depend on:

- GB structure (fluid form + thickness)
- Diffusive properties of intergranular fluid
- Mechanism & kinetics of interfacial reactions

Quantifying IPS = resolving these unknowns

……. via experiments !!!!!!

Experiments on NaCl



Diffusion Control:

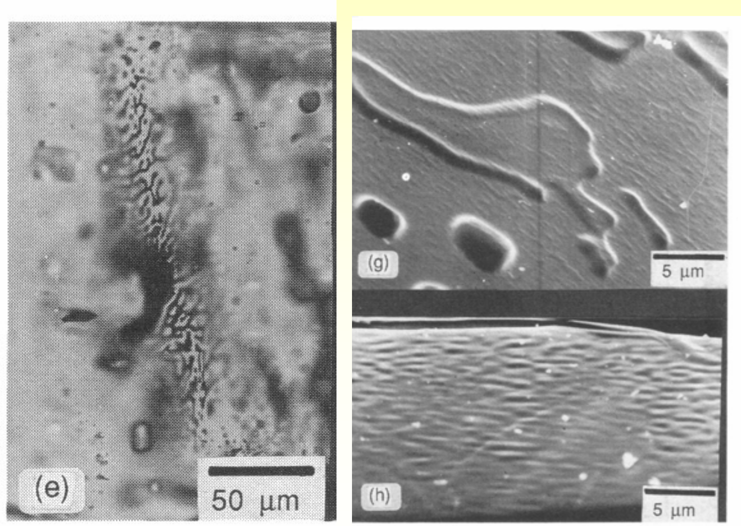
$$\dot{\varepsilon}_d = [DCS] \cdot \frac{\sigma_e}{d^3} \cdot f_d(\phi)$$

$DCS \approx 10^{-19}$ $m^3\ s^{-1}$ at 20°C

$\Delta H \approx 24.5$ kJ/mol

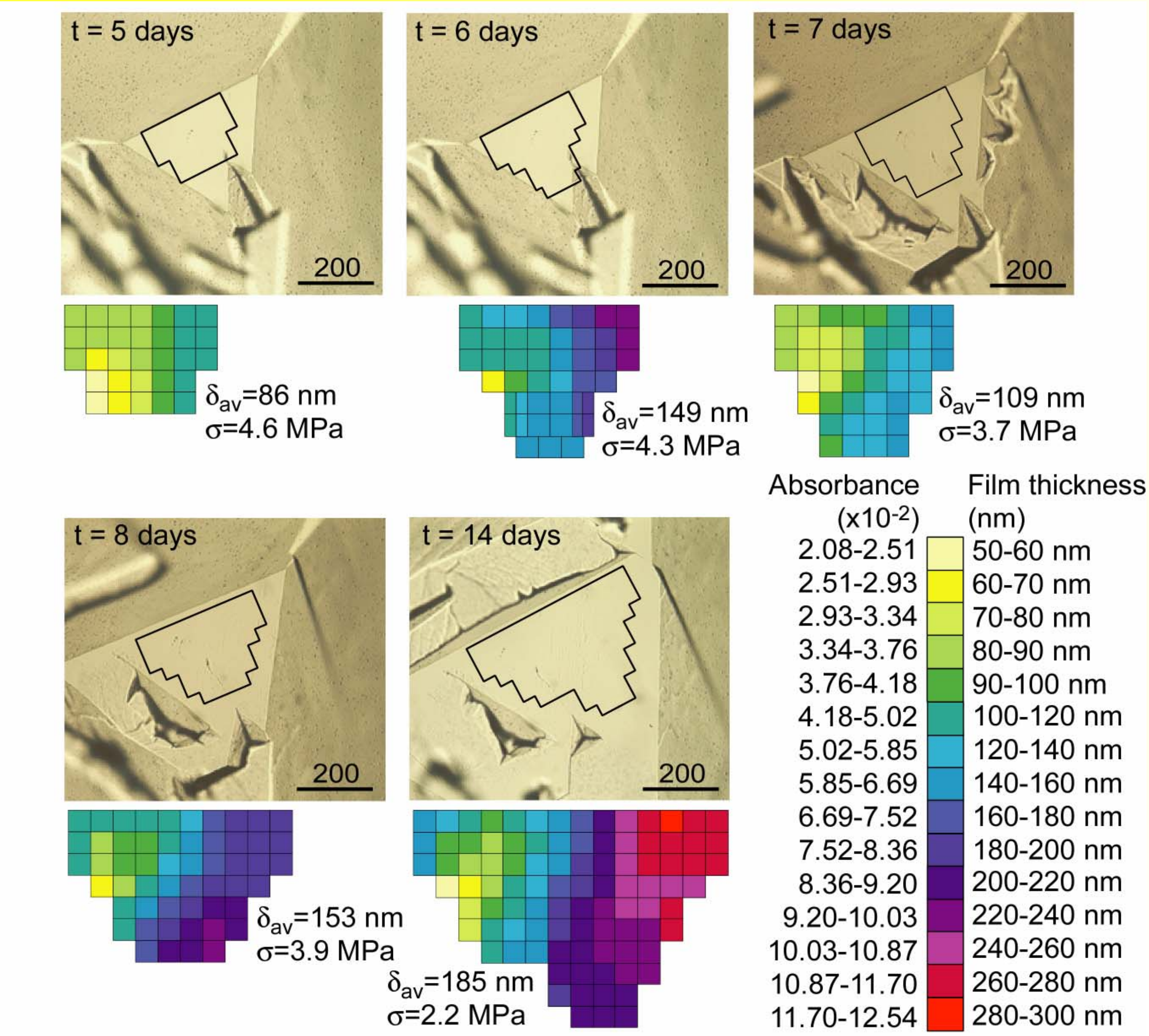
Spiers et al (1990)

But.....what was the grain boundary structure (S) during deformation ?



Post-mortem gb structure

NaCl-CaF$_2$ contact



Absorbance ($\times 10^{-2}$)		Film thickness (nm)
2.08-2.51	🟨	50-60 nm
2.51-2.93	🟨	60-70 nm
2.93-3.34	🟩	70-80 nm
3.34-3.76	🟩	80-90 nm
3.76-4.18	🟩	90-100 nm
4.18-5.02	🟩	100-120 nm
5.02-5.85	🟦	120-140 nm
5.85-6.69	🟦	140-160 nm
6.69-7.52	🟦	160-180 nm
7.52-8.36	🟪	180-200 nm
8.36-9.20	🟪	200-220 nm
9.20-10.03	🟪	220-240 nm
10.03-10.87	🟪	240-260 nm
10.87-11.70	🟥	260-280 nm
11.70-12.54	🟥	280-300 nm

FTIR
Micro-Mapping

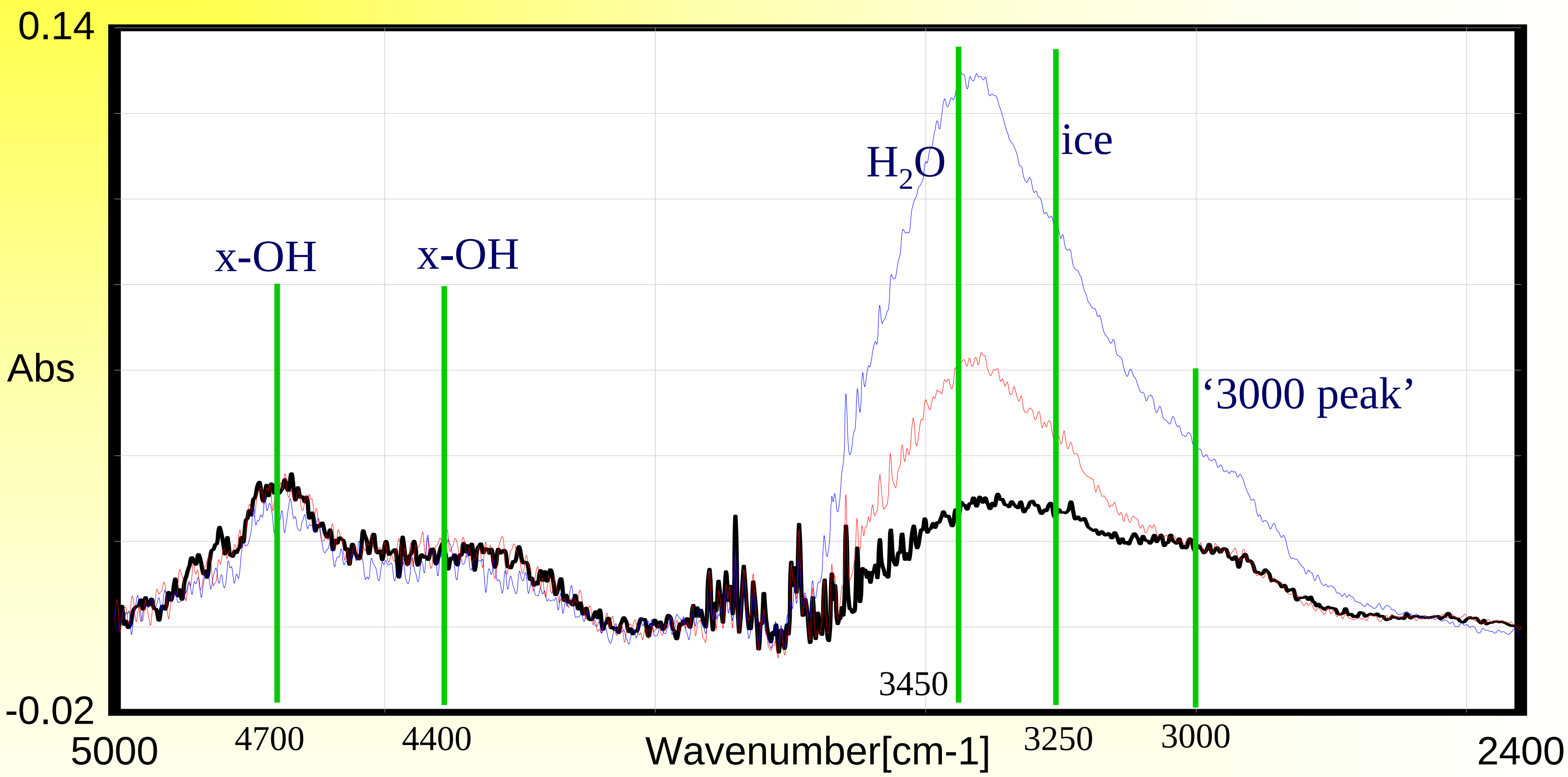
[111] orientation

De Meer et al (2005)

Mean fluid thickness ~100 nm

Spectra for individual points

(S= 300,140 & 55 nm, top down)



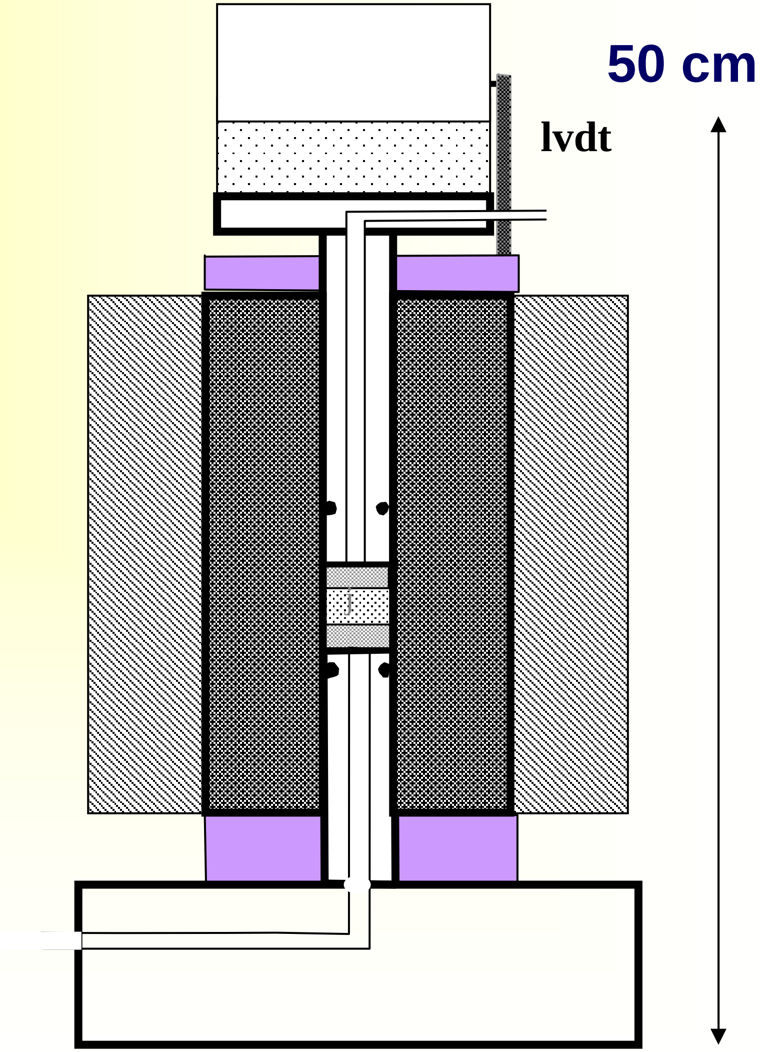
Change in peak position reflects changes in hydrogen bonding and water structure in thin fluid film; ‘3000 peak’ related to hydrohalite ($NaCl·2H_2O$)??

NaCl contacts undergoing IPS:
Summary

- Rough evolving gb structure on (111) & (100) contacts
- Mean fluid thickness S = 20-200 nm
- Charged surfaces >> structuring of H_2O
- Dissolution rate data yield DCS >>>
  - $D \approx D_{bulk}/10$..... at room T ($DS \approx 10^{-18}$ m^3 s^{-1})
- D consistent with compaction, bicrystal, surface force data

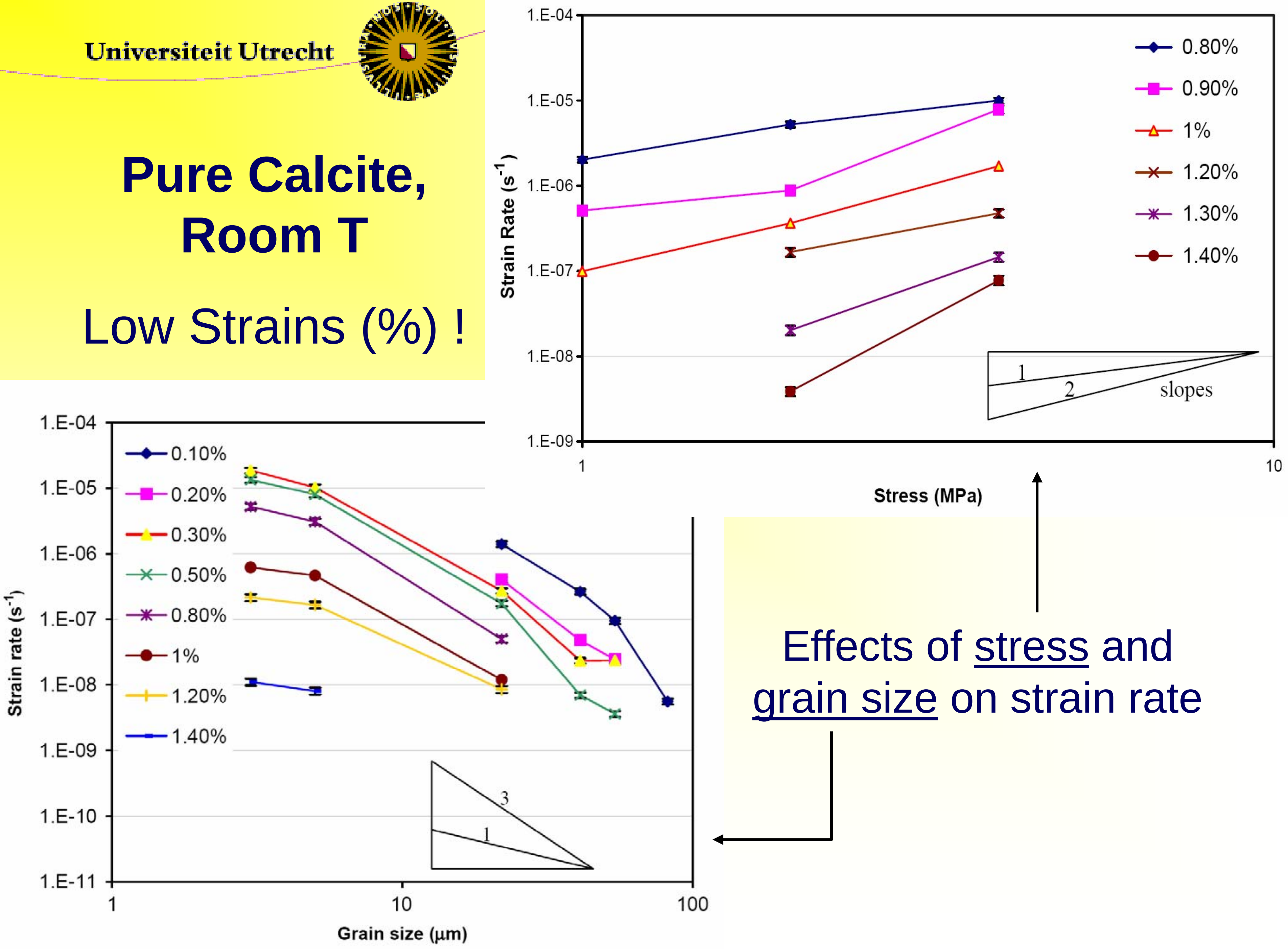
Compaction experiments on calcite (Zhang & Spiers 2005)

Temp:	20 - 150 °C
Eff stress:	4-40 MPa
Pore fluid:	$CaCO_3$ solution Added Mg^{2+}, PO_4^{3-}
Materials:	Crushed limestone Pure calcite (5-50 μm)



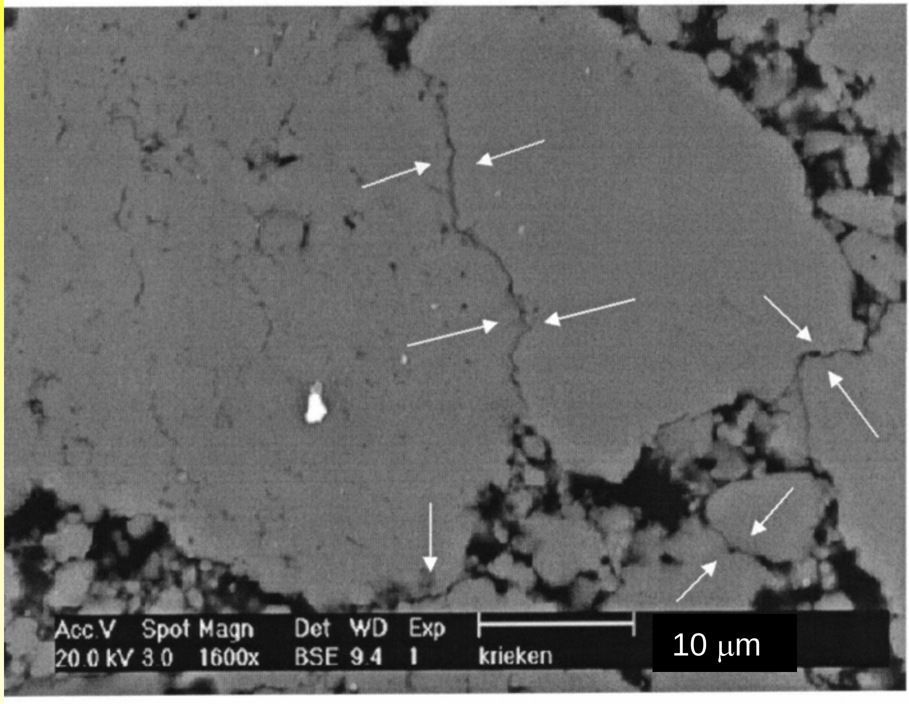
Pure Calcite, Room T

Low Strains (%) !



Effects of <u>stress</u> and <u>grain size</u> on strain rate

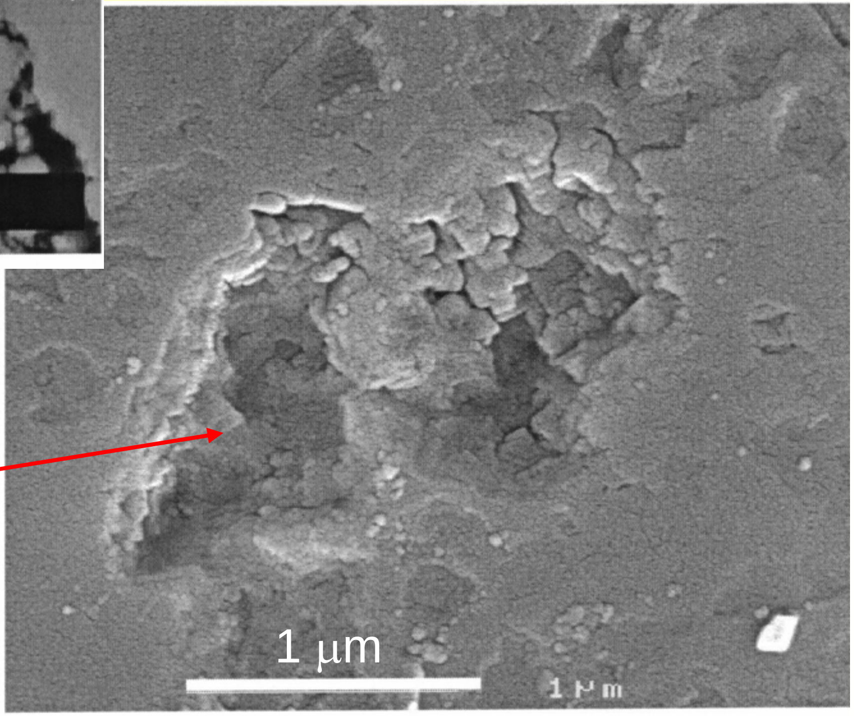
Calcite: Microstructures



Crushed limestone 28-45 μm

σ_e = 30 MPa, T = 150 °C

P_f = 15 MPa



Dissolution pit in cleaved calcite flake

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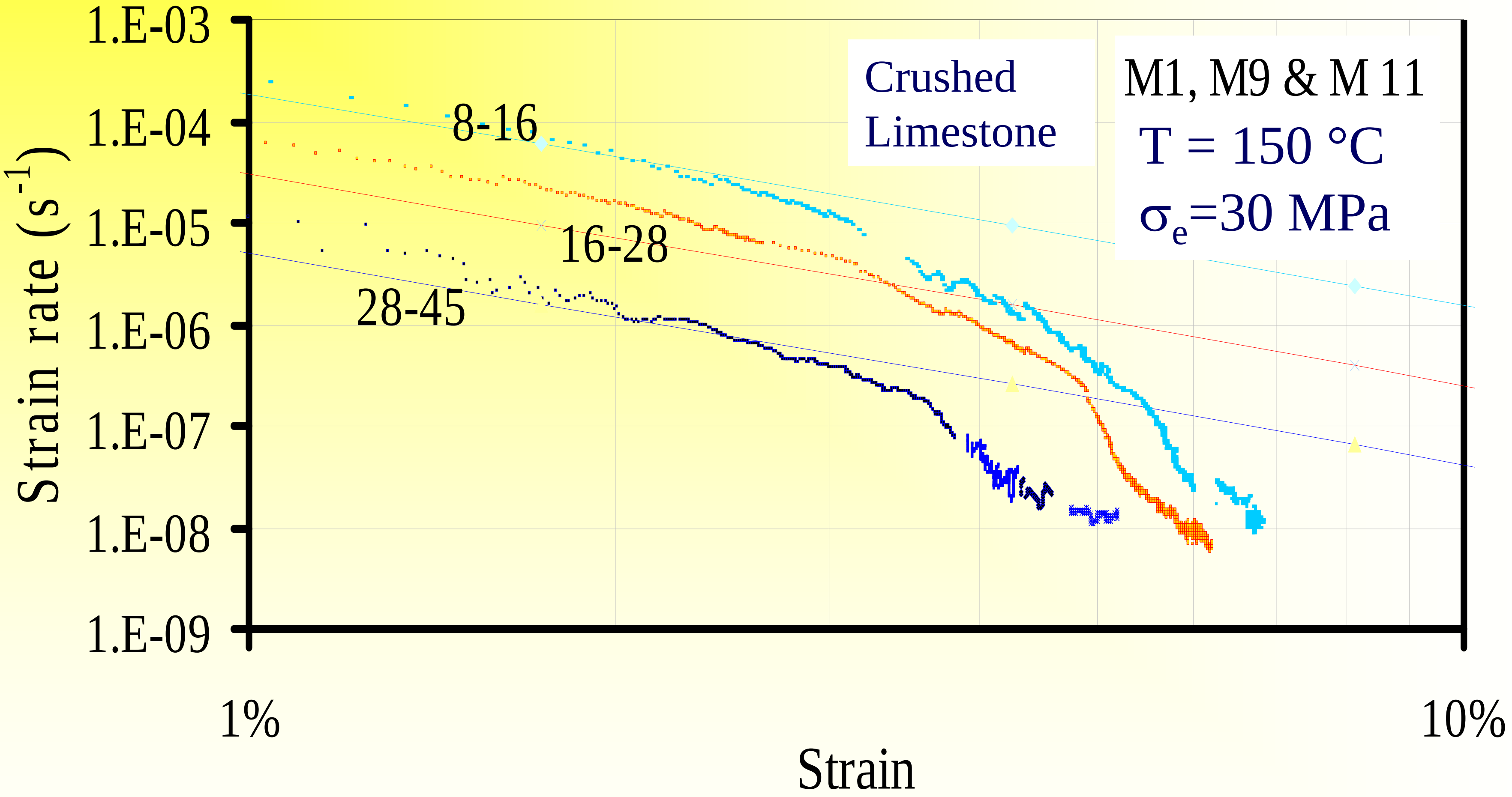
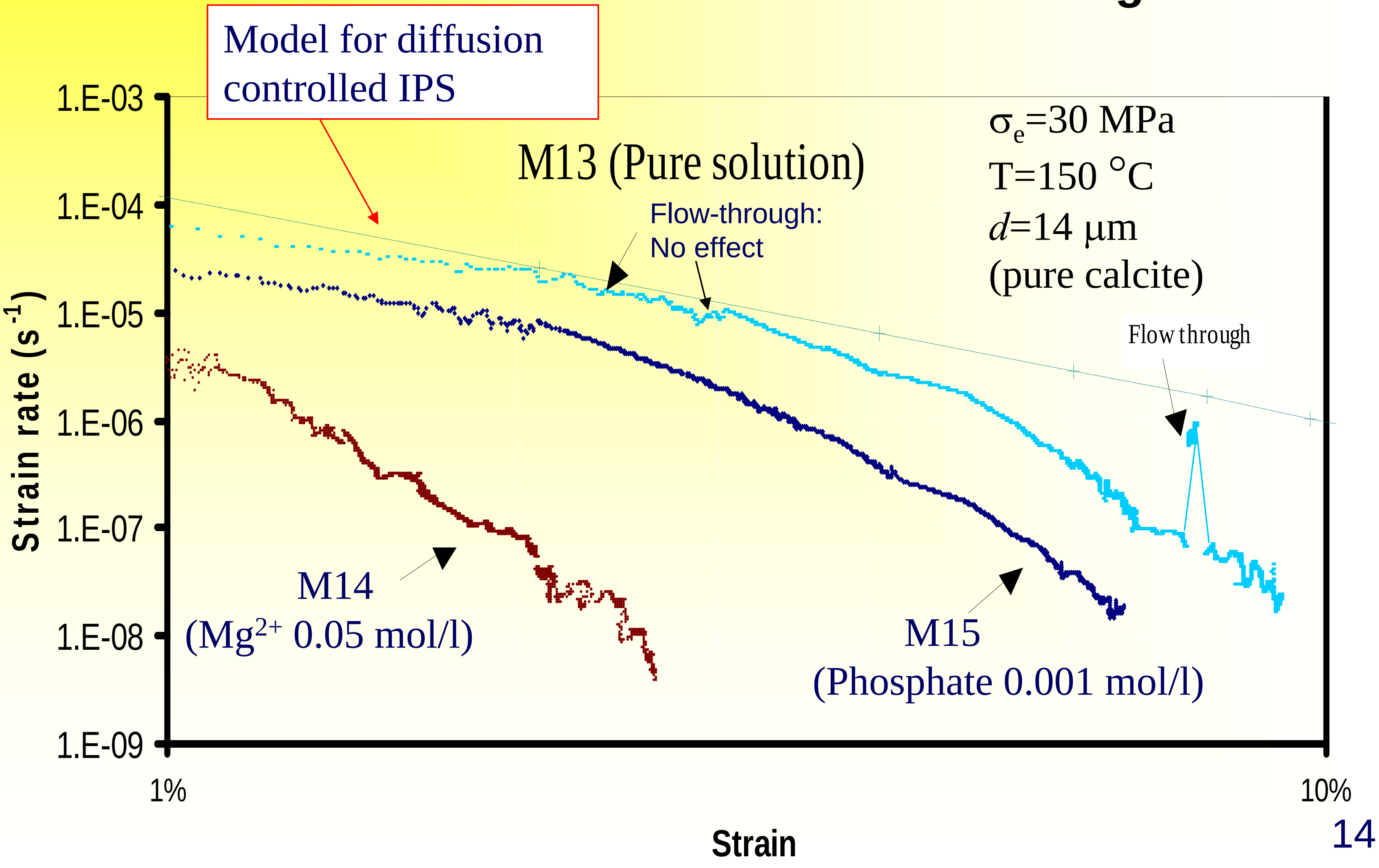
Calcite: Experiment vs. Theory



Solid lines: Model predictions for diffusion controlled IPS with $DS = 1.8 \times 10^{-18}\ m^3\ s^{-1}$

Calcite: Effect of Mg^{2+}, phosphate and flow-through



Model for diffusion controlled IPS

M13 (Pure solution)

Flow-through:
No effect

σ_e=30 MPa
T=150 °C
d=14 µm
(pure calcite)

Flow through

M14
(Mg^{2+} 0.05 mol/l)

M15
(Phosphate 0.001 mol/l)

Summary for calcite

- IPS obtained
- Active grain boundary structure probably rough
- Diffusion control in pure systems, low strain
  ($DS = 1.8 \times 10^{-18}$ m^3 s^{-1})
- Precipitation control in impure systems, high strains
- Mg^{2+} and PO_4^{3-} strongly reduce compaction rates

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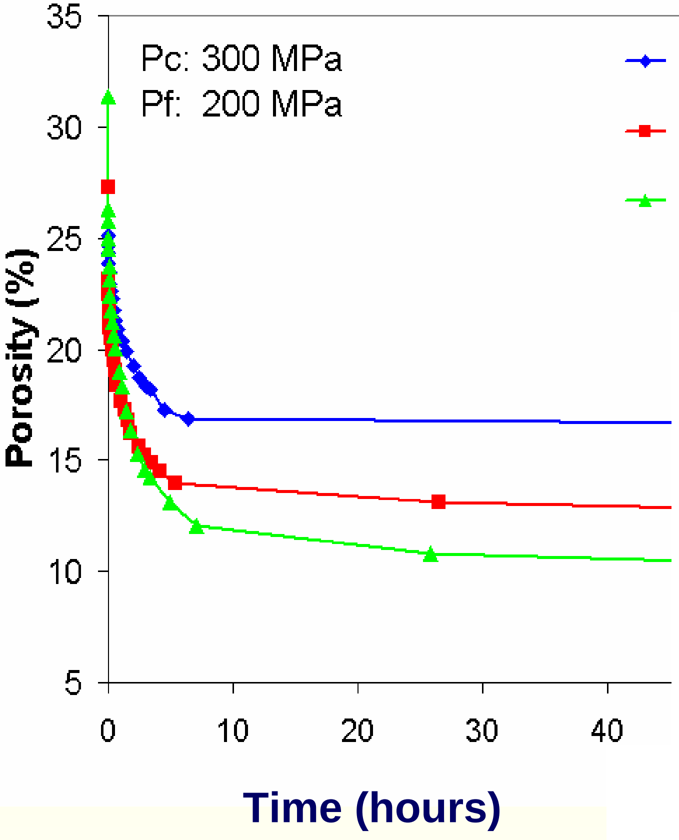
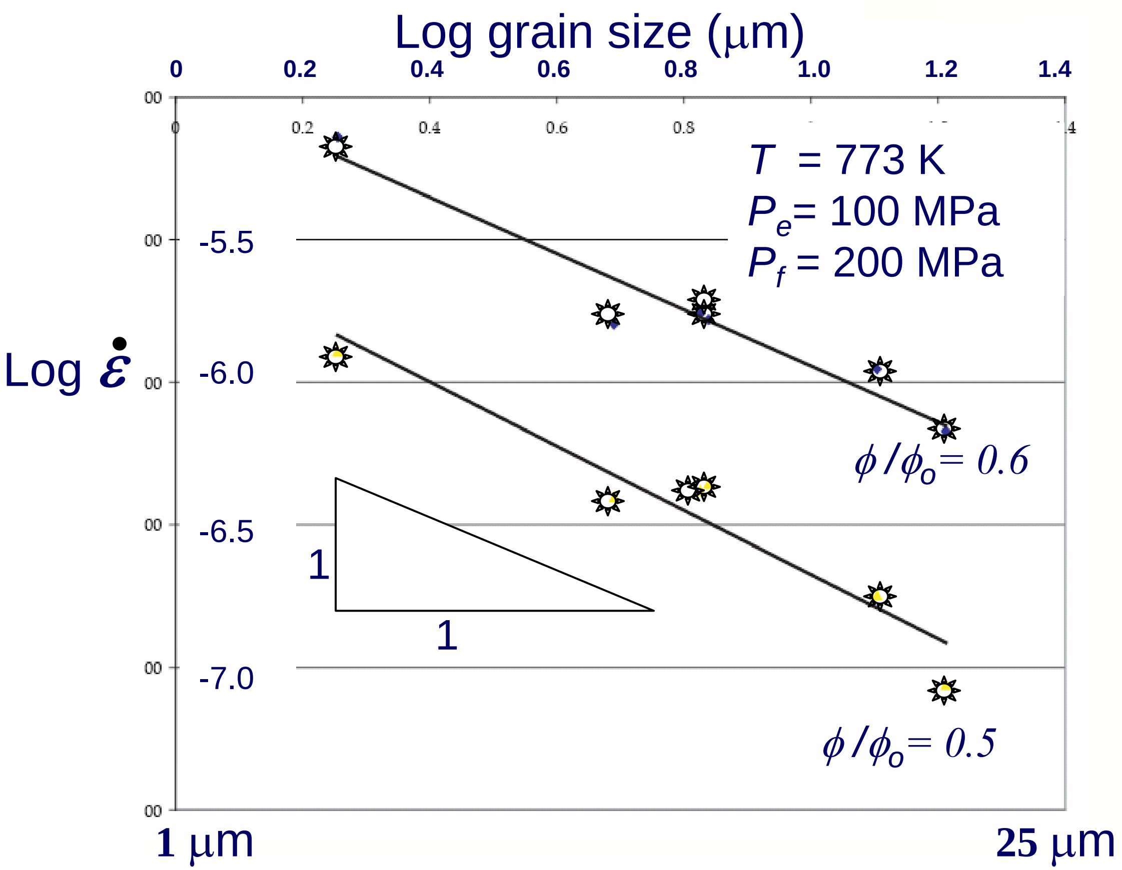
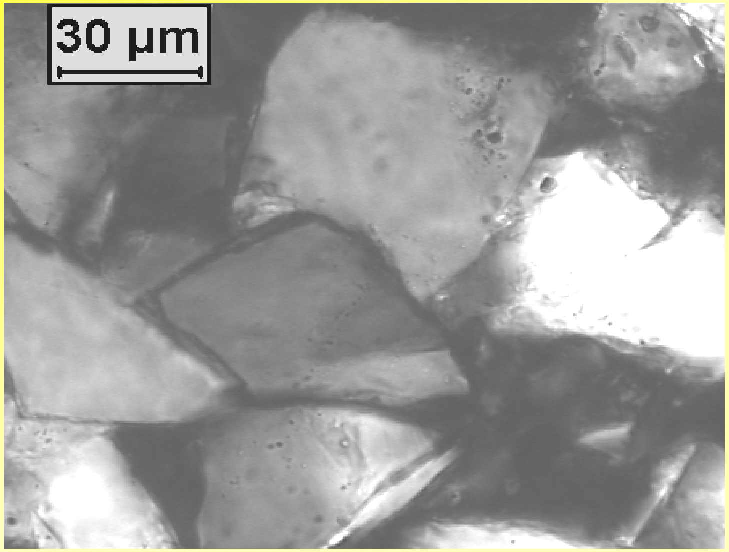
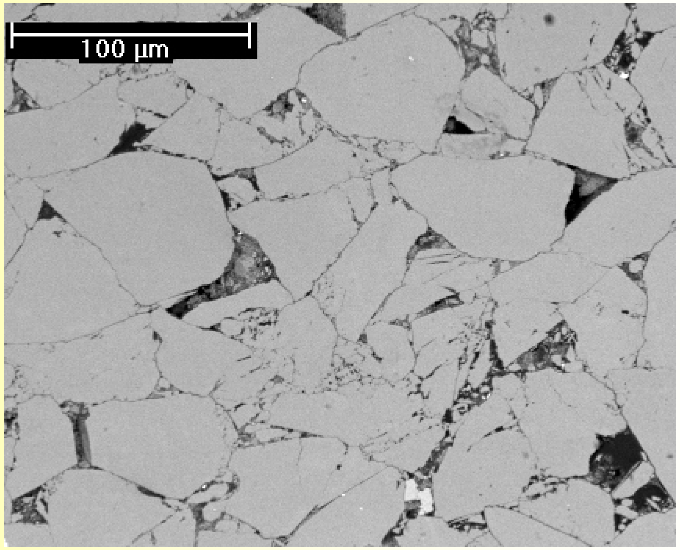
Isostatic compaction tests on quartz sand (400-600 °C)

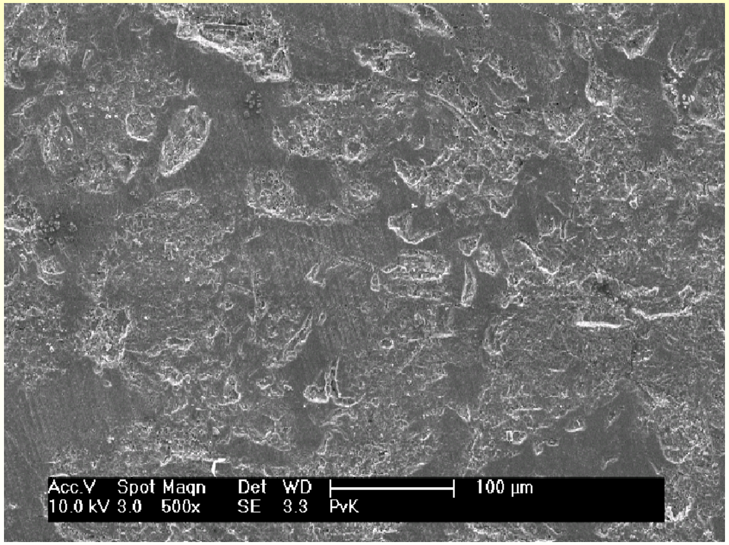


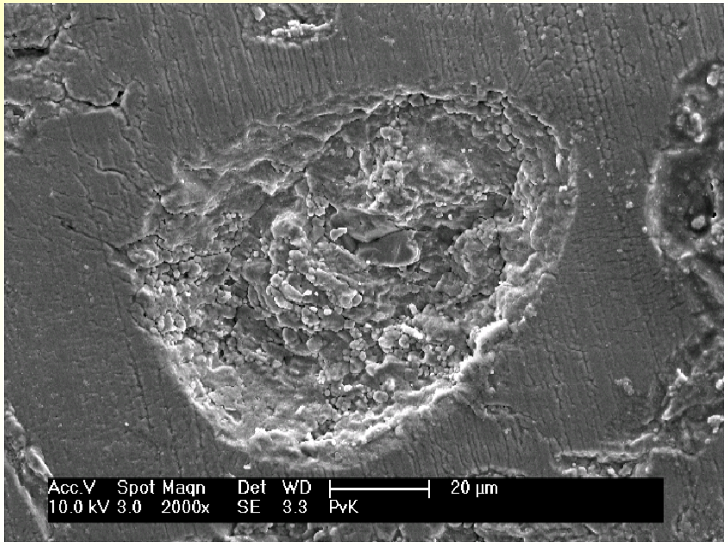


Quartz sand: Microstructures

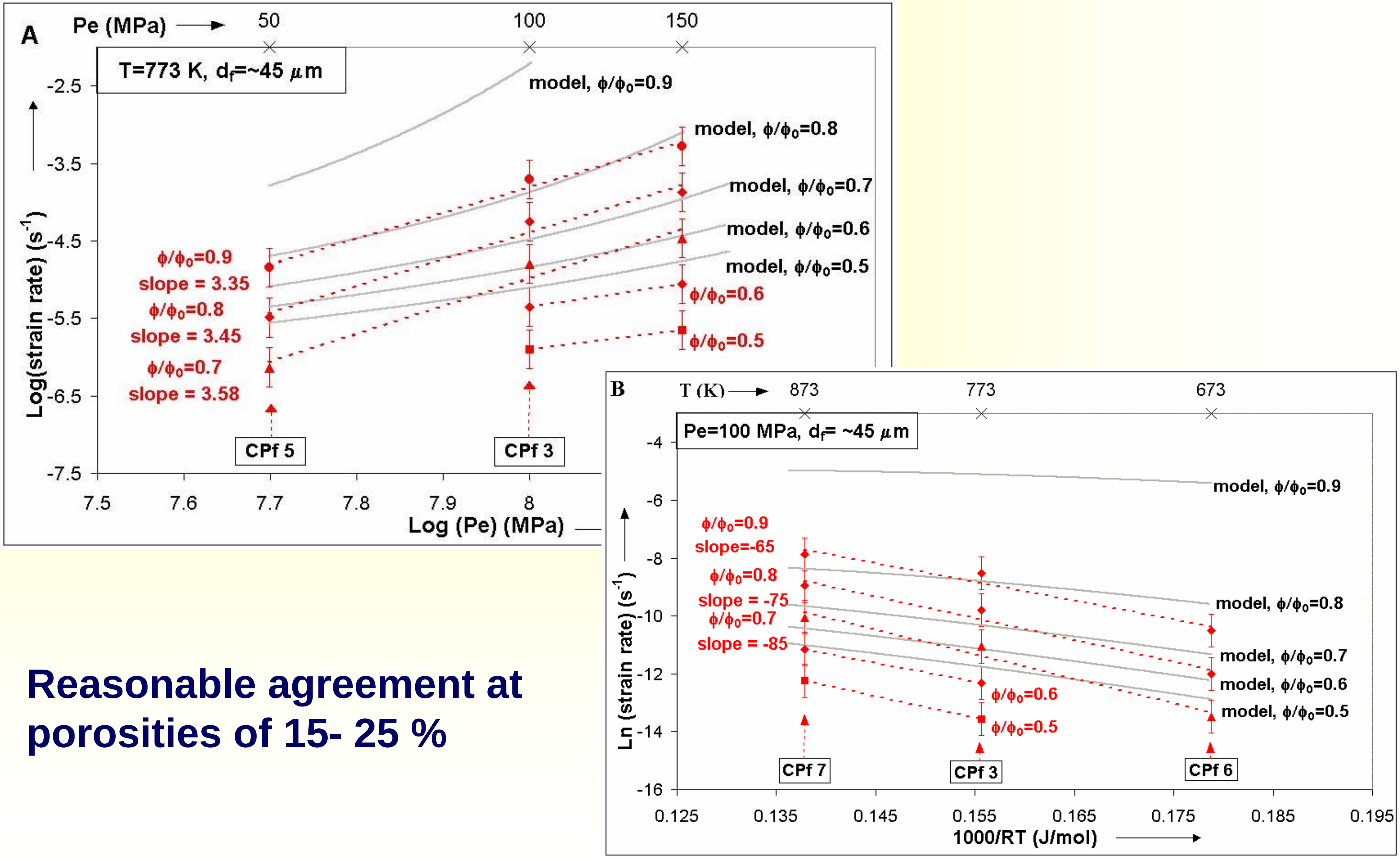








Creep data v. dissolution controlled IPS model



Reasonable agreement at porosities of 15- 25 %

Summary for quartz

- IPS obtained at 400-600 ºC
- Active grain boundary structure probably rough
- Still some contact microcracking at 400-500 ºC
- Dissolution control offers best explanation for rates

General inferences and questions

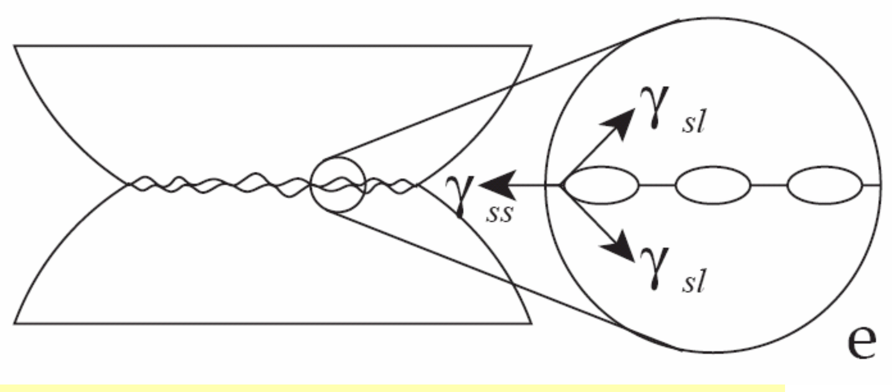
- **Rough, non-equilibrium gb structure seems widespread**

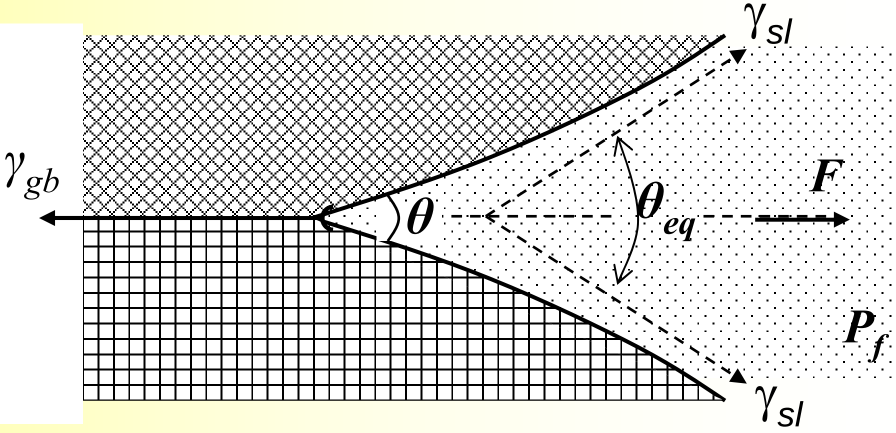
- **Salt:** Diffusion controlled IPS (gb fluid 20-200 nm thick)

- **Calcite + quartz:** Diffusion control unlikely in nature
  (rough gb's, high *D*, reaction control, impurity effects)

- **Extrapolated lab laws for quartz + calcite too fast: WHY?**
  Grain boundary healing >>> yield stress for IPS ?

Criterion for healing a rough grain boundary



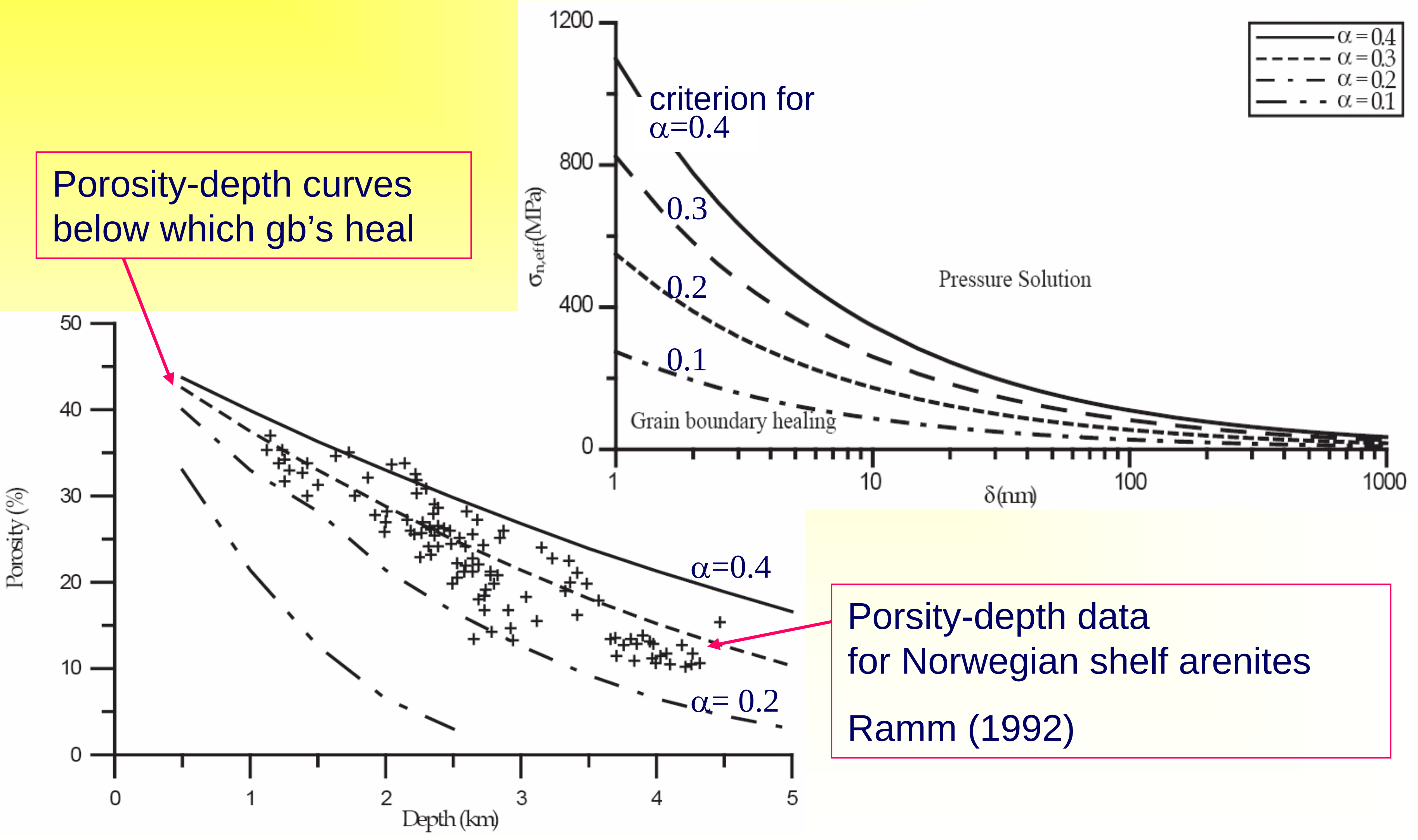


$$\frac{2\gamma_{sl}}{\delta}\Omega_s\left(\cos\frac{\theta}{2}-\cos\frac{\theta_{eq}}{2}\right)-\frac{\left[\left(\sigma_n-P_f\right)/\alpha\right]^2}{2E}\Omega_s > 0$$

$$\left(\sigma_n-P_f\right)<\sigma_{crit}=2\alpha\sqrt{E\frac{\gamma_{sl}}{\delta}\left(\cos\frac{\theta}{2}-\cos\frac{\theta_{eq}}{2}\right)}$$

GB healing predictions for quartz rocks

Porosity-depth curves below which gb's heal



Porsity-depth data for Norwegian shelf arenites

Ramm (1992)

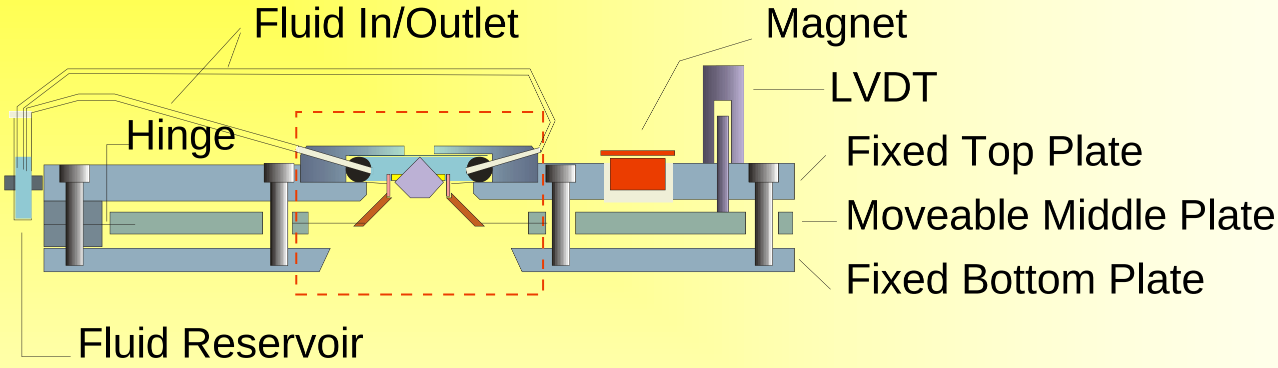
(δ = 50 nm, 25°C/km, 2200 kg/m^3, hydrostatic P_f)

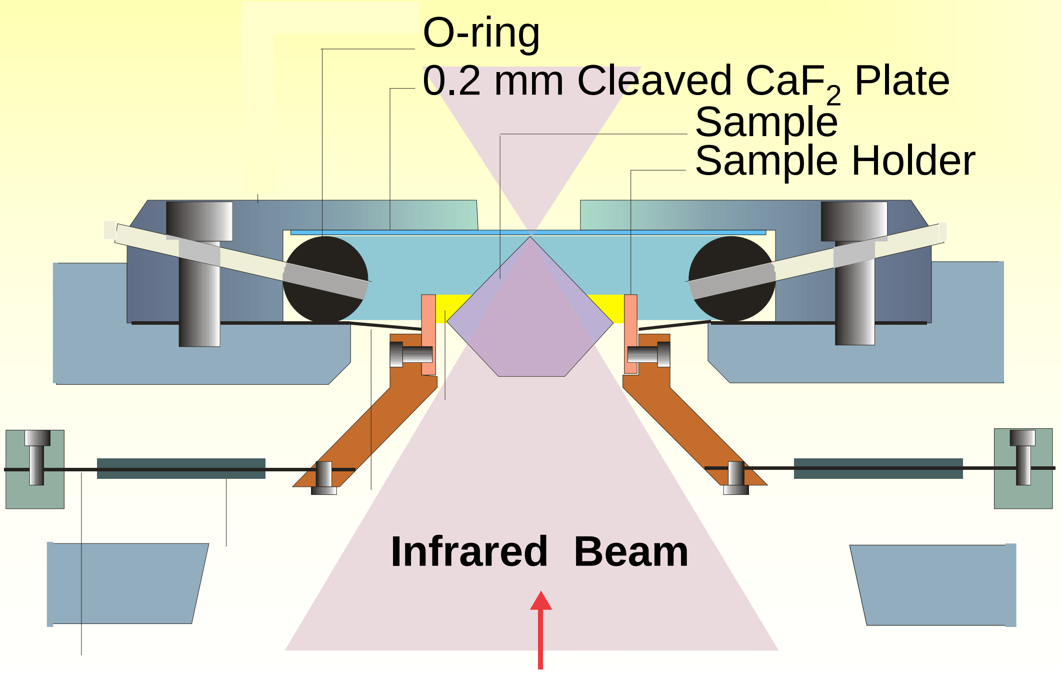
Conclusion:

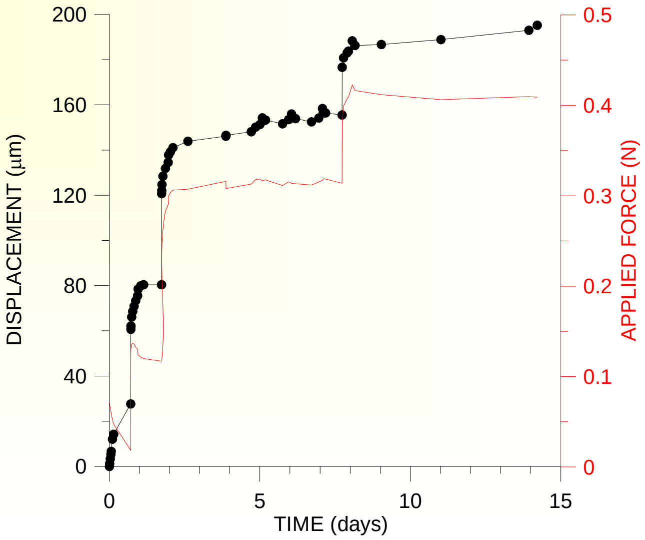
Perhaps gb healing
is a serious possibility for
limiting pressure solution in rocks !!

Thank you for your attention !!!

In-situ FTIR spectroscopy

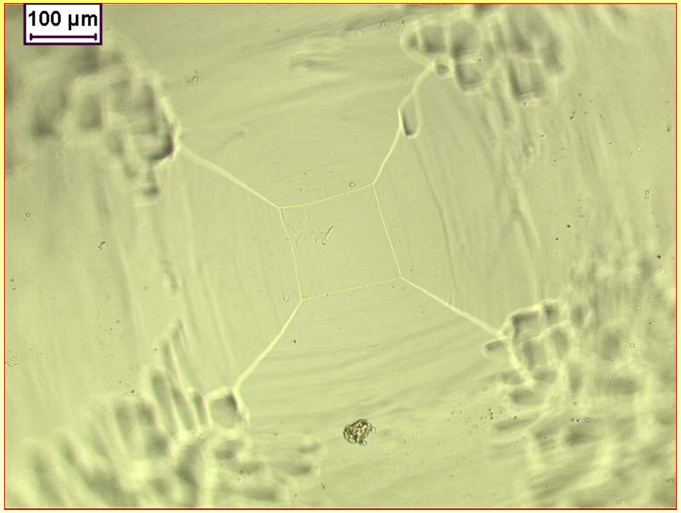


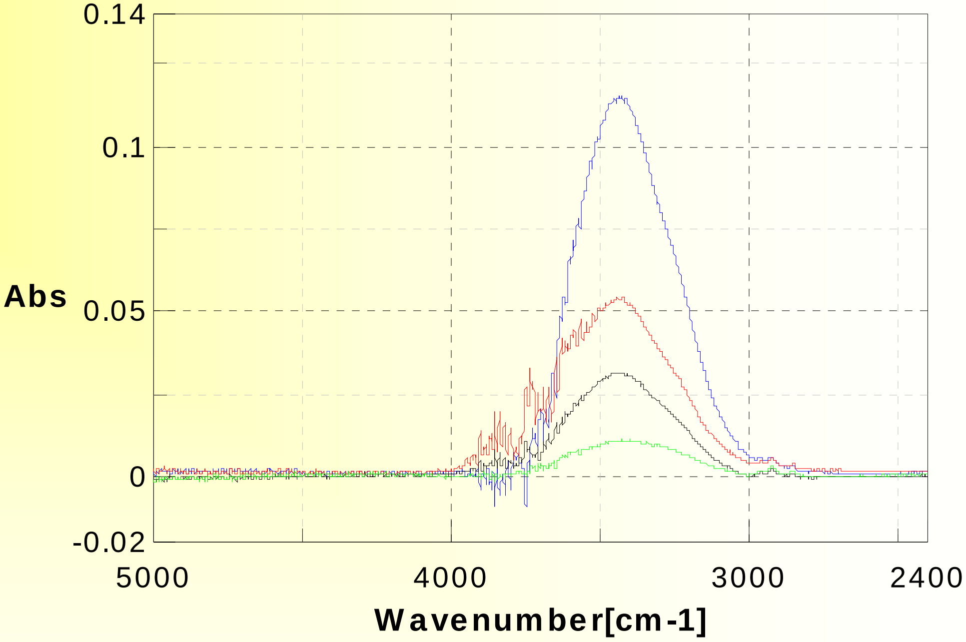




NaCl loaded in [100] direction

(S= 270,135, 75 & 25 nm, top down)

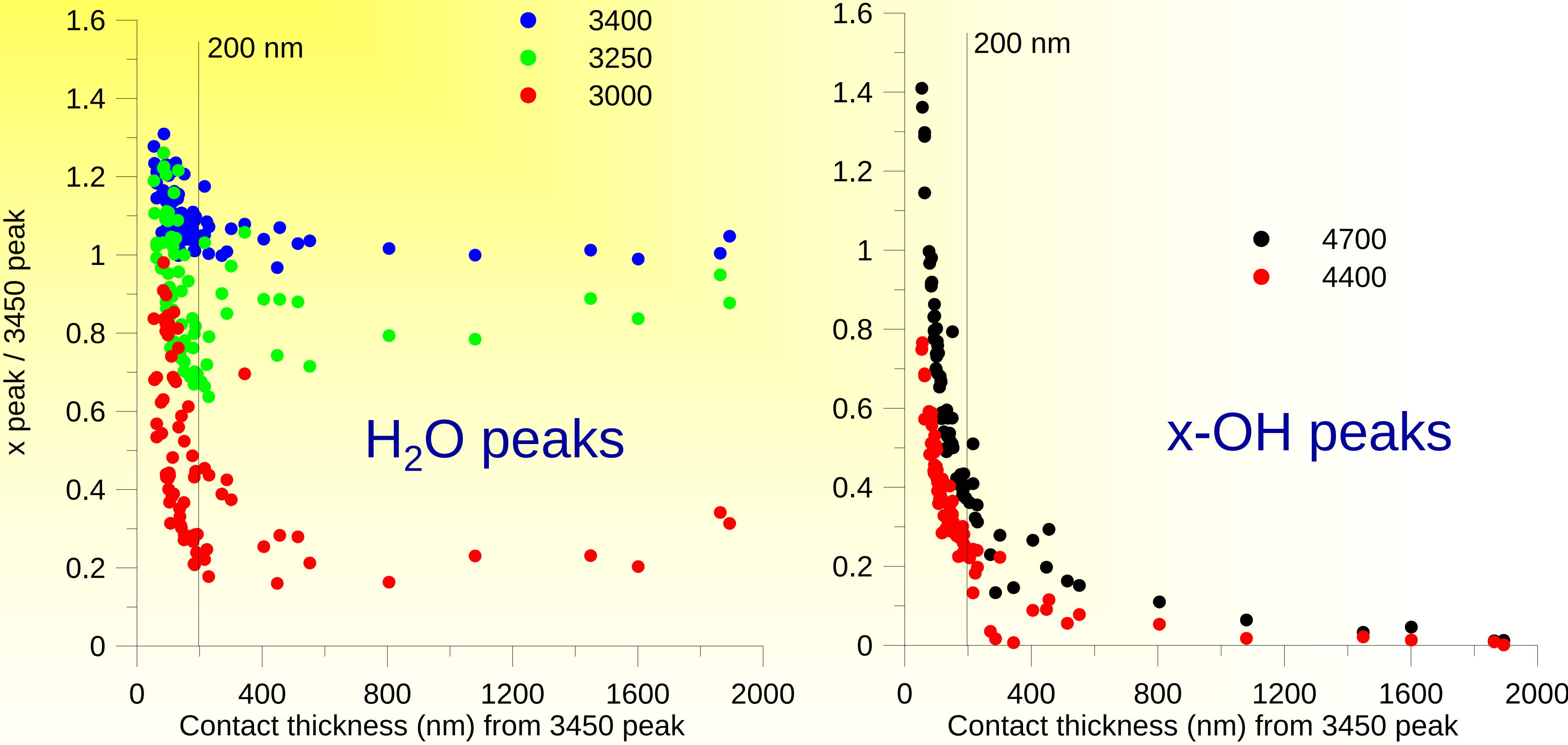




Contact stress ~ 4 MPa

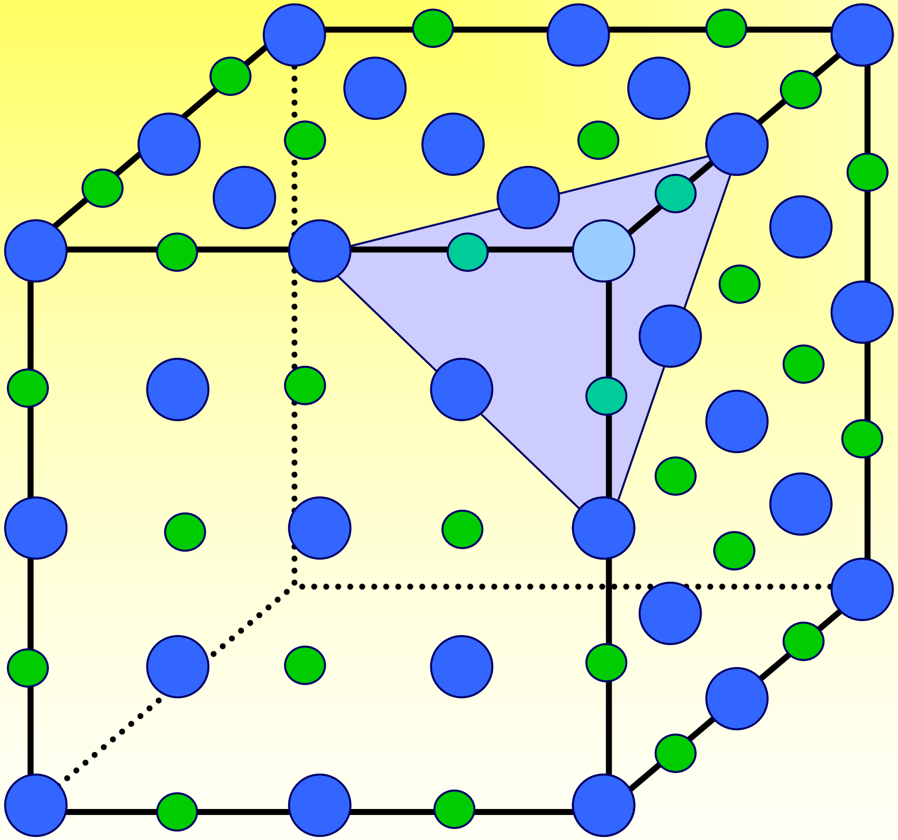
Mean fluid thickness after 5 days ≈ 50 nm

Loading in [111] direction



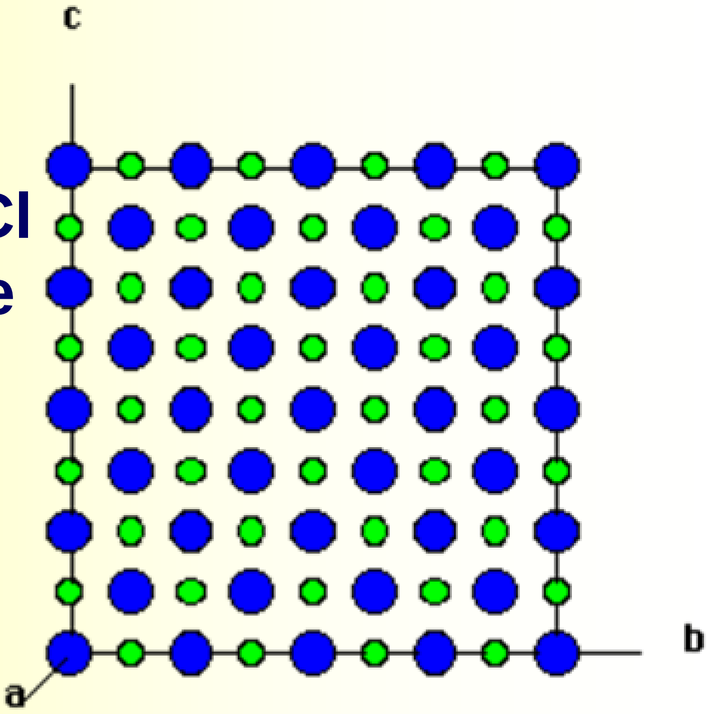
3450 peak is “normal” peak for NaCl solutions

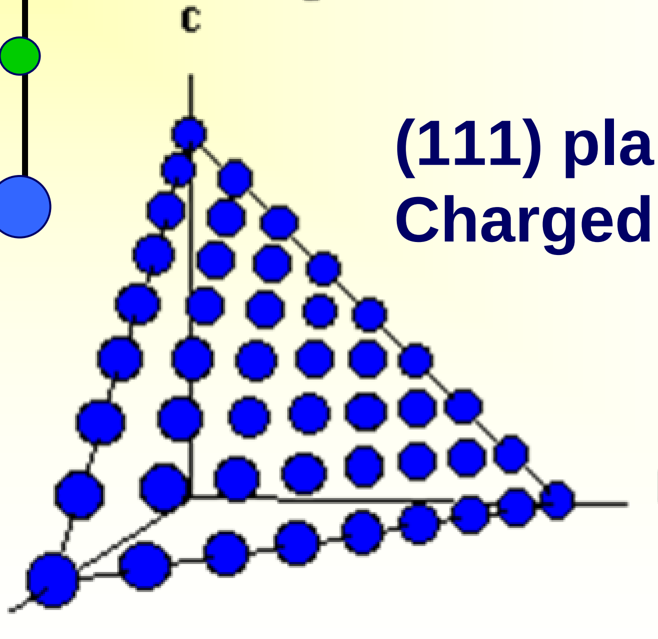
NaCl Structure



● Na^+ ● Cl^-

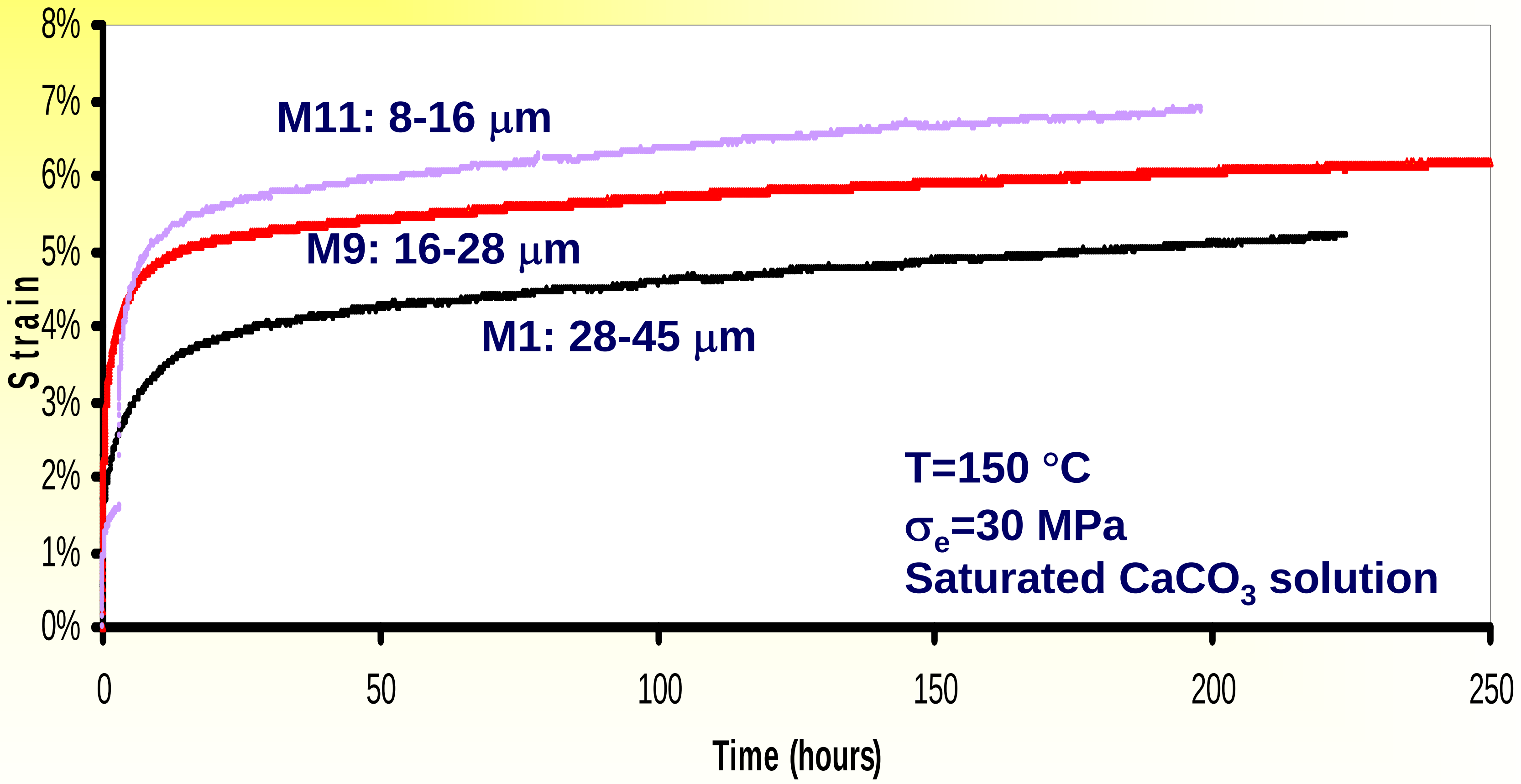
(100) plane of NaCl
No surface charge



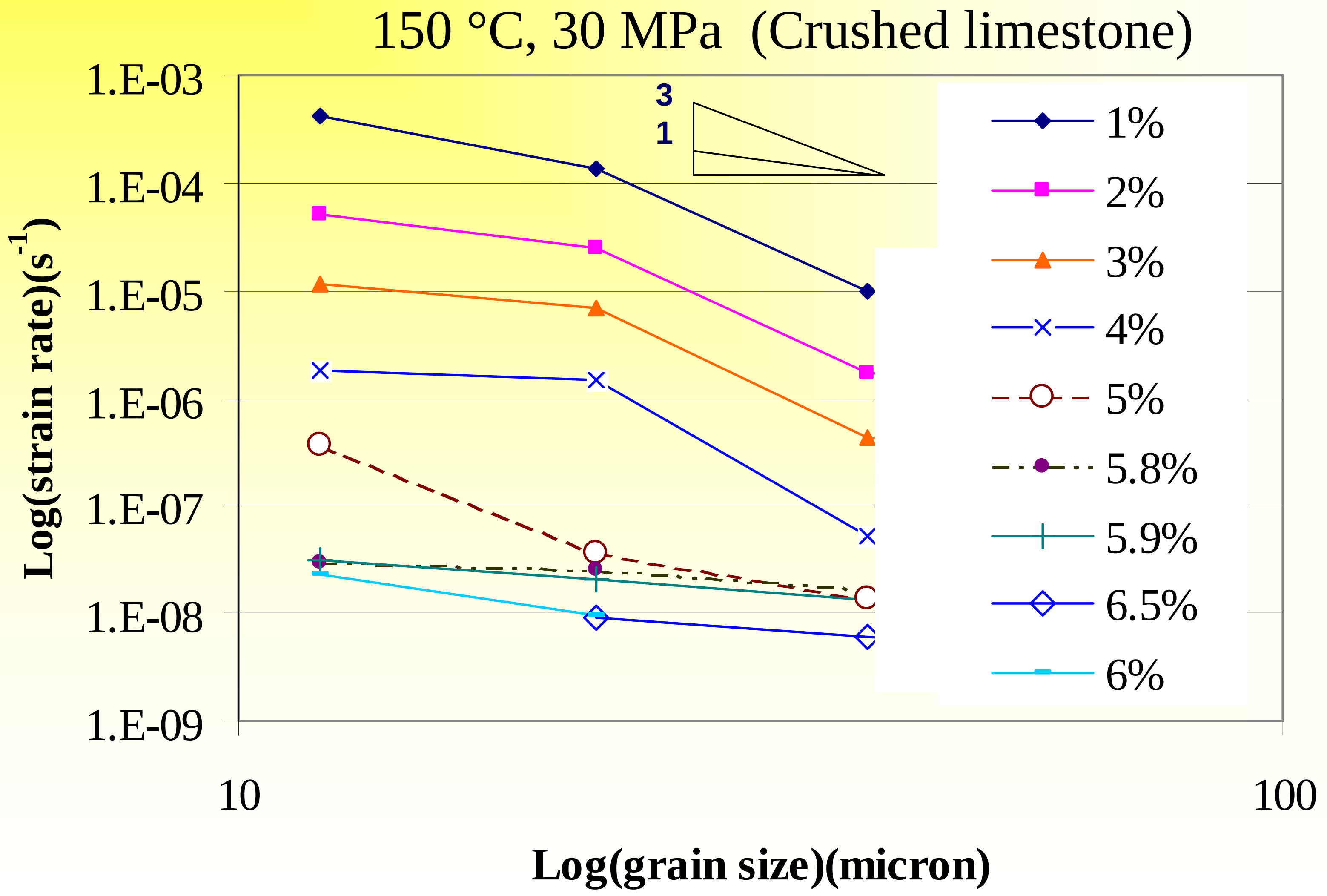


(111) plane of NaCl
Charged surface

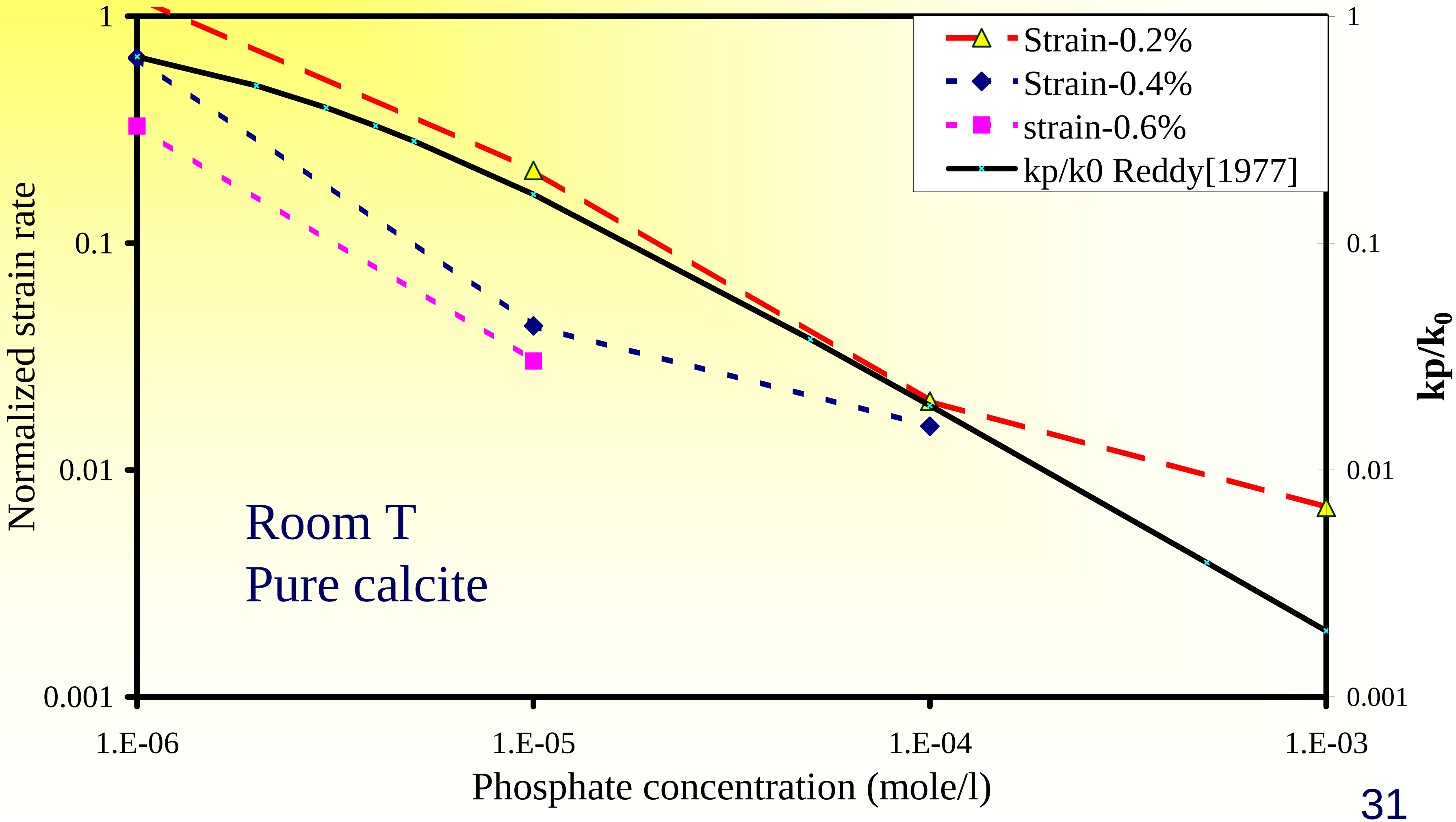
Effect of Grain size : Crushed limestone



Strain rate v. grain size at fixed strains (%)



Effect of phosphate concentration vs. precipitation rate coefficient



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Compaction experiments on quartz sand (Niemeijer et al 2002)

Conditions:

- Temperature: 400-600 º C
- Isostatic P: 300 MPa
- Fluid P: 150-250 MPa