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Mineral nucleation in nanopores and on flat surfaces: Understanding interfacial energy controls using in situ synchrotron techniques

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Mineral nucleation on flat surfaces: Thermodynamics of carbonate mineral heterogeneous nucleation

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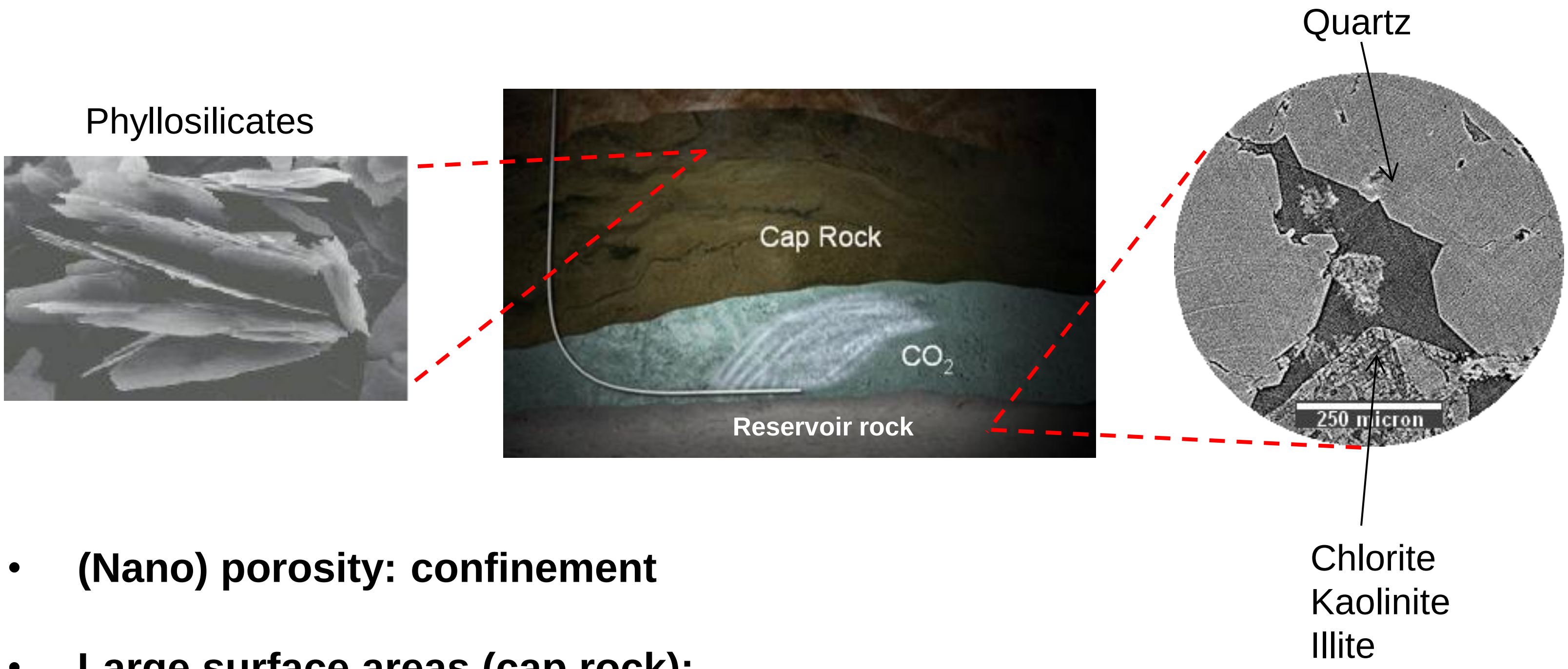
Complex geological media offer loci for nucleation



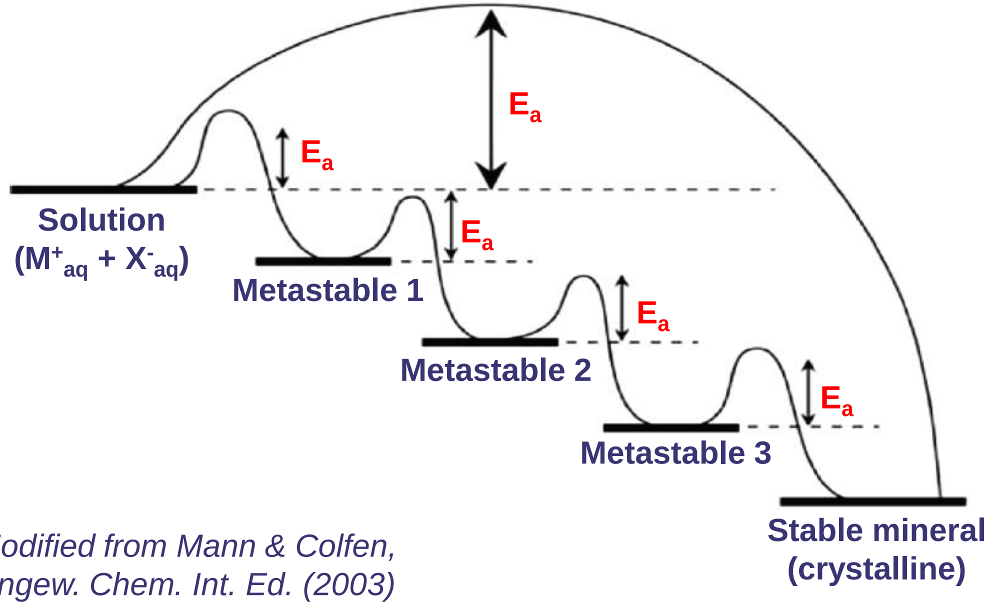
- **(Nano) porosity: confinement**
- **Large surface areas (cap rock): ubiquitous presence of mineral surfaces**
- **High salinity, high organic content**
- **High pressure and temperature**

How does the presence of a mineral substrate affect the thermodynamics of mineral nucleation?

Thermodynamics and kinetics of nucleation

Nucleation rate

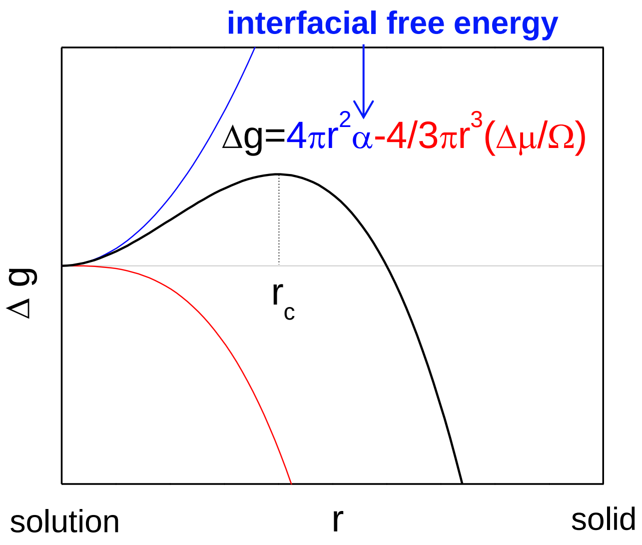
$$J_n = Ae^{\left(\frac{-\Delta G_c}{kT}\right)} = \overset{\text{kinetic}}{\boxed{A_0 e^{-\left(\frac{E_a}{kT}\right)}}}\;\overset{\text{thermodynamic}}{\boxed{e^{-\left(\frac{B\alpha^3}{\sigma^2}\right)}}}$$



Modified from Mann & Colfen, Angew. Chem. Int. Ed. (2003)

The interplay of thermodynamic (free energy landscape) and kinetic factors (ion pairing, de-hydration barriers, cluster sticking coefficients..) drive mineral nucleation and growth

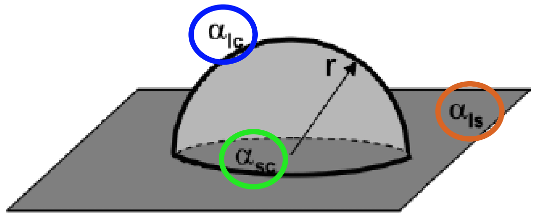
Thermodynamics and kinetics of nucleation



kinetics

Nucleation rate, J_n: $\ln(J_n) = \ln(A) - \frac{B\alpha'^3}{\sigma^2}$

thermodynamics



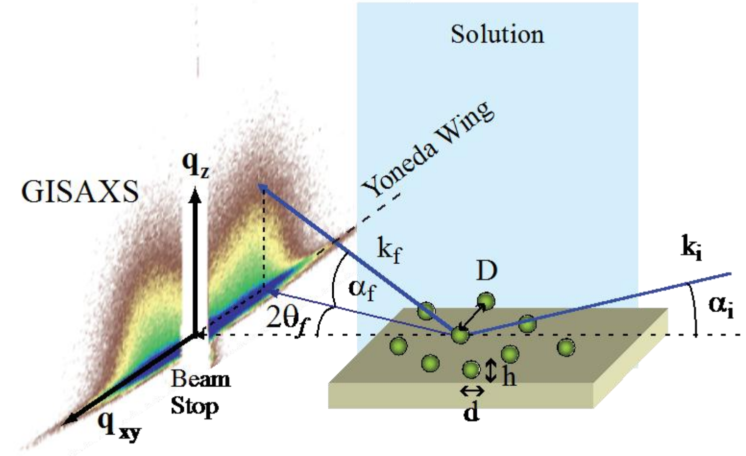
$$\alpha' = \alpha_{lc}\{1-(\alpha_{ls}-\alpha_{sc})/2\alpha_{lc}\}$$

from DeYoreo and Vekilov (2003)

- If $\alpha_{ls} > \alpha_{sc}$ then $\alpha' < \alpha_{lc} \longrightarrow$ Heterogeneous nucleation
- If $\alpha_{ls} = \alpha_{sc}$ then $\alpha' = \alpha_{lc} \longrightarrow$ Cross-over homogeneous/ heterogeneous nucleation
- If $\alpha_{ls} < \alpha_{sc}$ then $\alpha' > \alpha_{lc} \longrightarrow$ Homogeneous nucleation

The interplay between the different interfacial energies will determine the nature of the nucleation process and the spatial distribution of the precipitate

Mineral nucleation on mineral surfaces: GISAXS

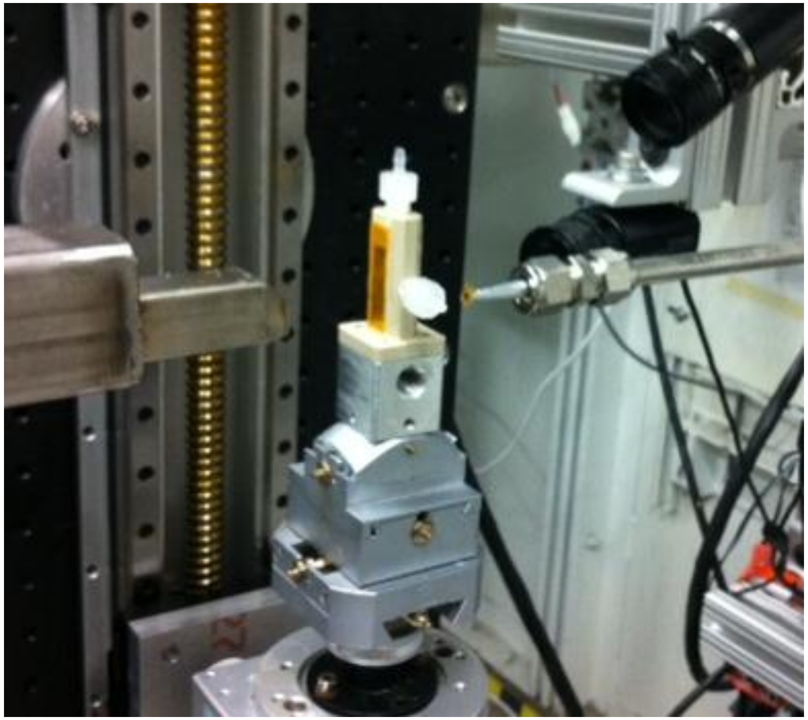


Jun and Waychunas, ES&T (2010)

- **Surface-sensitive technique**

- **Resolves particle sizes ranging from 0.5 to 500 nm**

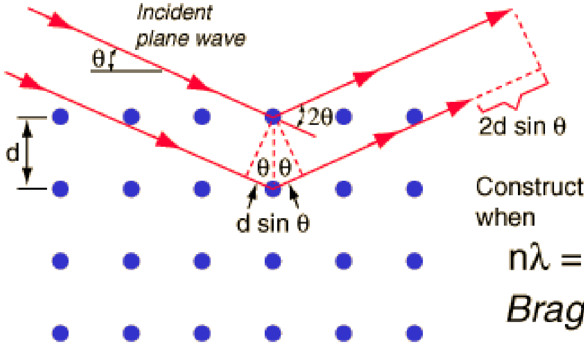
- **Gives size and shape information of very first nucleated $CaCO_3$ particles on mineral surfaces**



12IDB – APS @ 12 KeV

Small Angle X-ray Scattering

X-ray Diffraction: Magnifying glass x 10^8



Constructive interference when

$$n\lambda = 2d \sin\theta$$

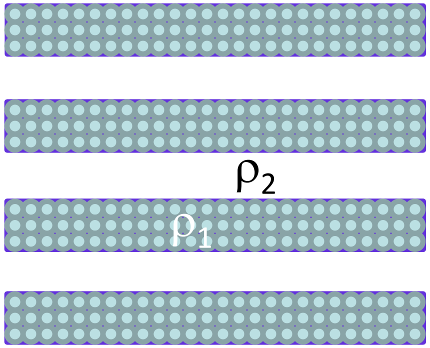
Bragg's Law

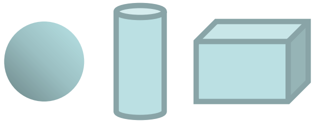
$$\sin\theta \downarrow \;\Rightarrow\; d \uparrow$$

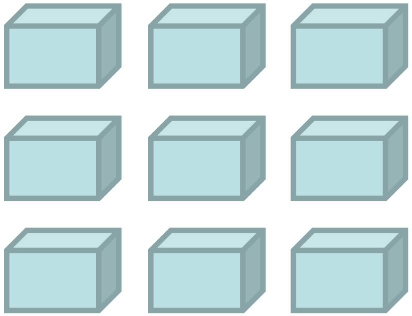
Small Angle X-ray Scattering: Magnifying glass x 10^6

$$I(q) \approx NV^2(\rho_1 - \rho_2)^2 P(q) S(q)$$

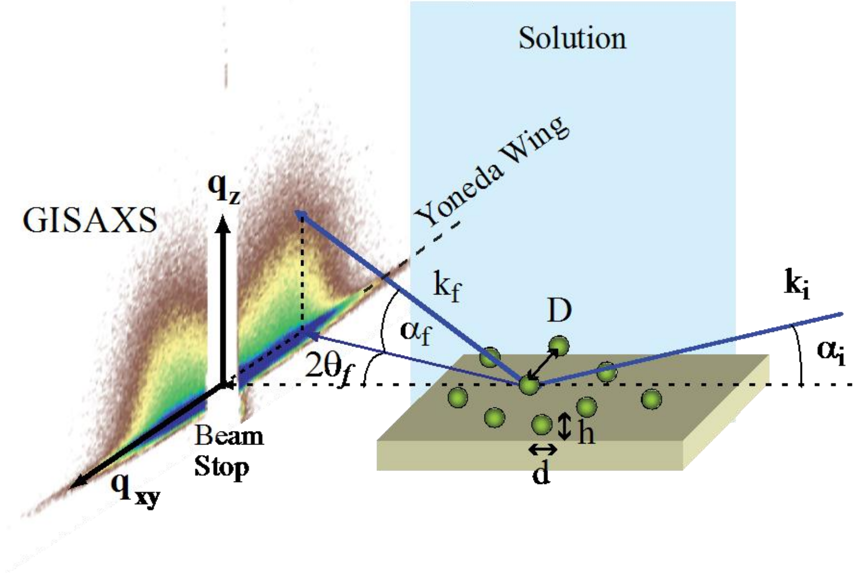
↑ intensity







Experimental conditions: $CaCO_3$ on quartz (100)

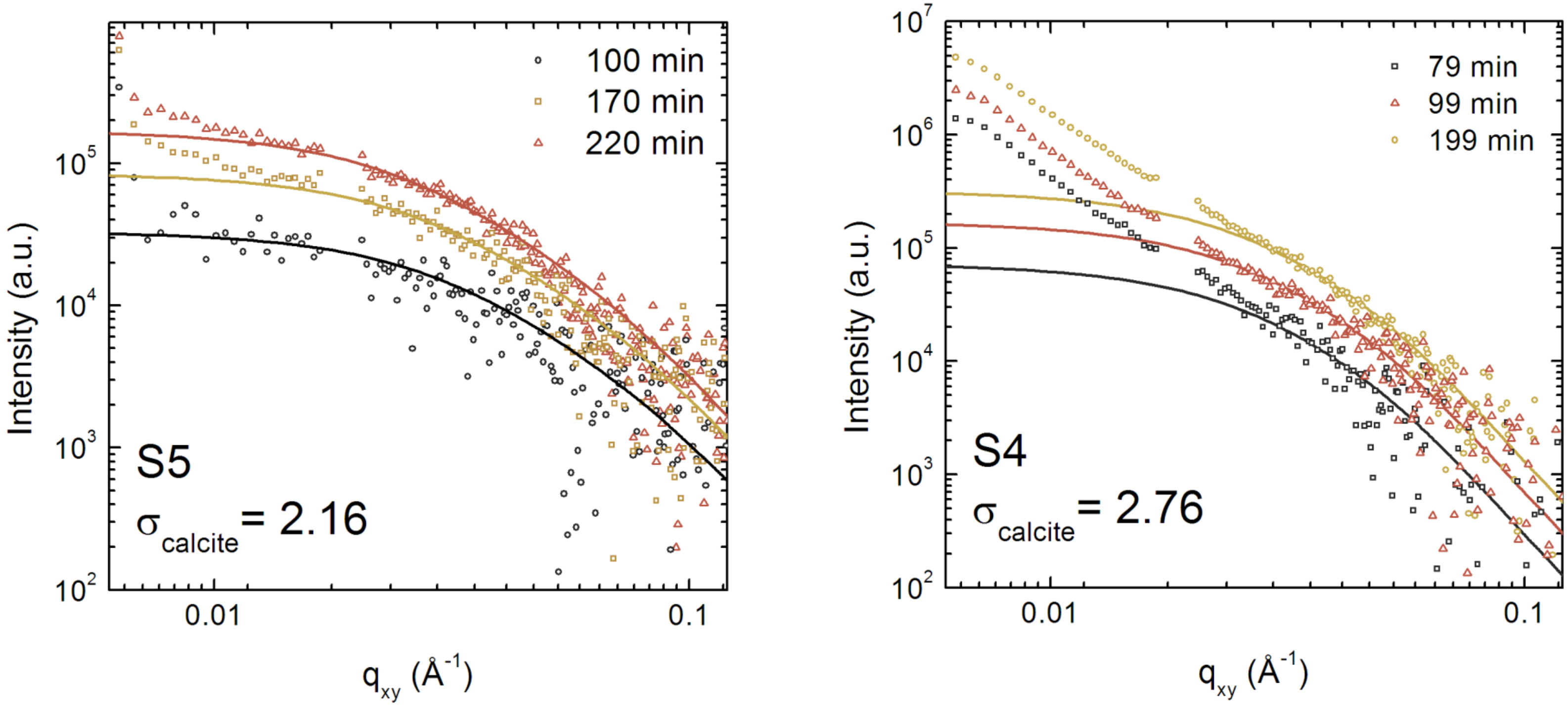


- **Experiments performed in an open system (constant σ) by keeping a constant flow over the substrate**

$$\sigma = \ln\left\{\frac{\left(Ca^{2+}\right)\left(CO_3^{\ 2-}\right)}{K_{spCaCO_3}}\right\}$$

SAMPLE	$[Ca^{2+}]$ (M)	$[HCO_3^-]$ (M)	pH	σ calcite ($\log_{10}$(IAP/Ks))	σ vaterite ($\log_{10}$(IAP/Ks))	σ ACC ($\log_{10}$(IAP/Ks))
S1	0.05	0.01	7.60	3.98(1.73)	2.67(1.59)	-0.35(-0.81)
S2	0.05	0.007	7.61	3.77(1.64)	2.46(1.5)	-0.44(-1.64)
S3	0.05	0.005	7.59	3.31(1.44)	2.0(1.3)	-0.64(-1.48)
S4	0.01	0.004	7.85	2.76(1.20)	1.45(1.06)	-0.88(-2.03)
S5	0.01	0.002	7.59	2.16(0.94)	0.85(0.8)	-1.14(-2.62)

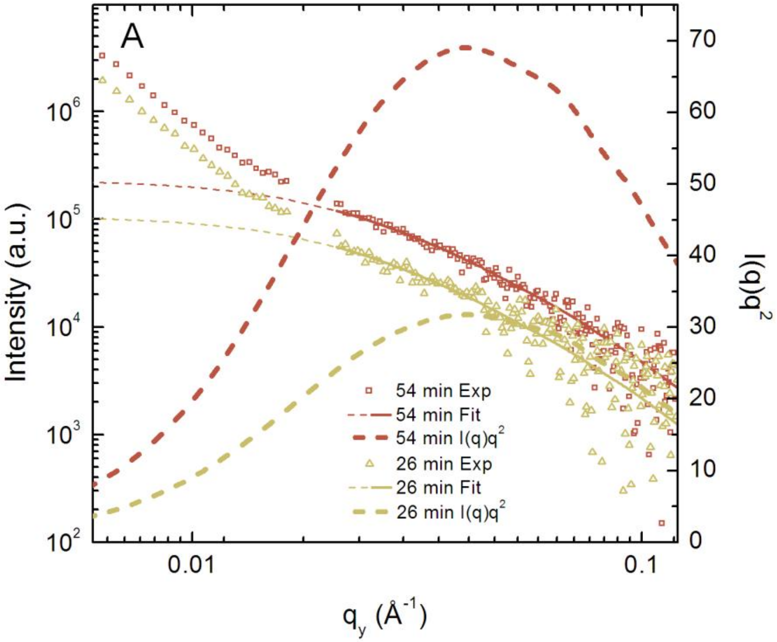
Carbonate nucleation on mineral surfaces: GISAXS



- **Particle scattering: ~2nm particles nucleated on quartz (100)**
- **Increase of the intensity with time with no change in size**

Carbonate nucleation on mineral surfaces: GISAXS

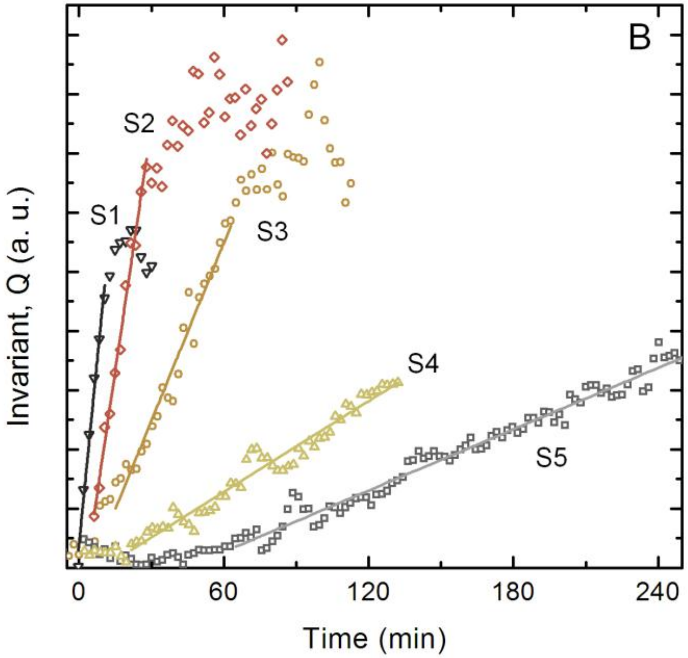
- **Total volume of $CaCO_3$ can be calculated using the invariant (Q), which in this case, with nucleation dominating over growth, will be proportional to the nucleation rate:**



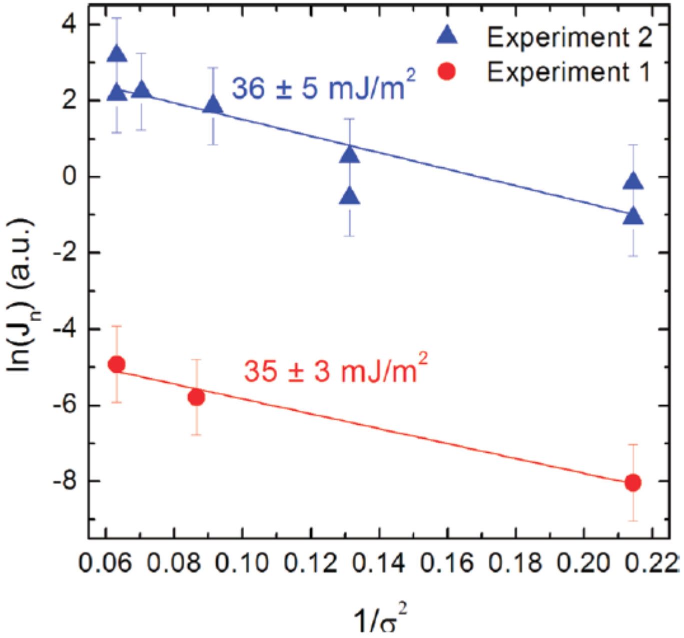
$$I(q) \approx NV^2(\rho_1 - \rho_2)^2 P(q)S(q)$$

$$Q = \int_{q_{\min}}^{q_{\max}} I(q)q^2 dq$$

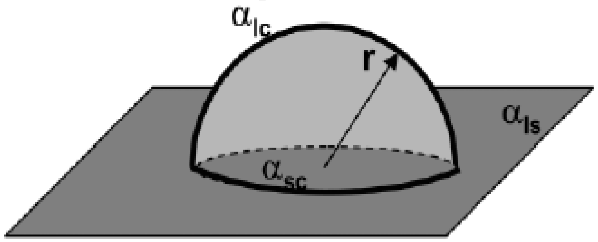
Carbonate nucleation on mineral surfaces: GISAXS



$$\ln(J_n) = \ln(A) - \frac{B\alpha'^3}{\sigma^2}$$



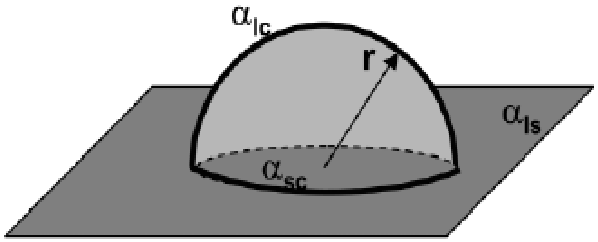
Hemispherical model



Carbonate nucleation on mineral surfaces: GISAXS

Calcite

Hemispherical model



$$\alpha' = \alpha_{lc}\{1-(\alpha_{ls}-\alpha_{sc})/2\alpha_{lc}\}$$

36 120* 360^+ 192 120*

* Average of values from:
- Bennema & Sohnel, J. Crys. Grow. (1990)
- Duffy & Harding, Langmuir (2004)
- Sohnel & Mullin, J. Crys. Grow. (1978)
- Liu & Lin, JACS (2003)

$^+$ Average value between the values in:
- Parks, Geophys. Res. Lett. (1984)
- Mizele et al. Surf. Sci. (1985)

(other values in the literature are well above or below this value)

Conclusions

- Grazing Incidence Small-angle X-ray scattering allows probing nucleation processes relevant to that carbonate mineralization in geological reservoirs. It allows obtaining interfacial energies from the systems under study.

- The obtained $CaCO_3$/quartz interfacial free energy is lower than the water/quartz interfacial free energy, showing a preference for nucleation on the substrate

- Hydrophobicity and surface mismatch will govern heterogeneous nucleation at the subsurface.

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Nucleation in confinement

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Dave Cole *Ohio State University, USA*

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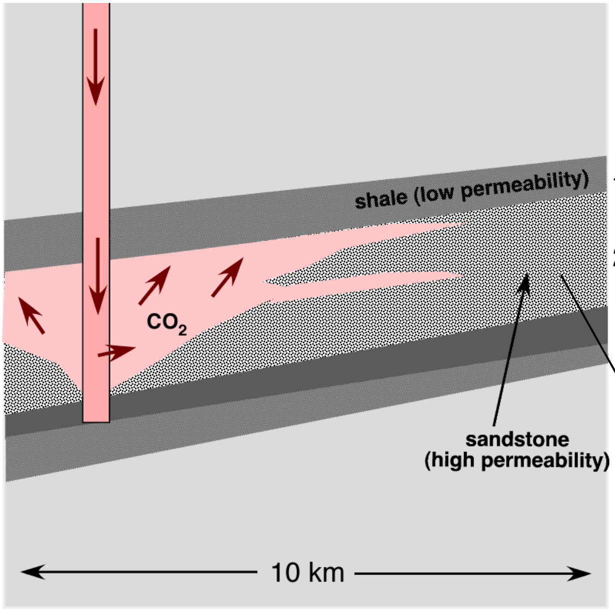
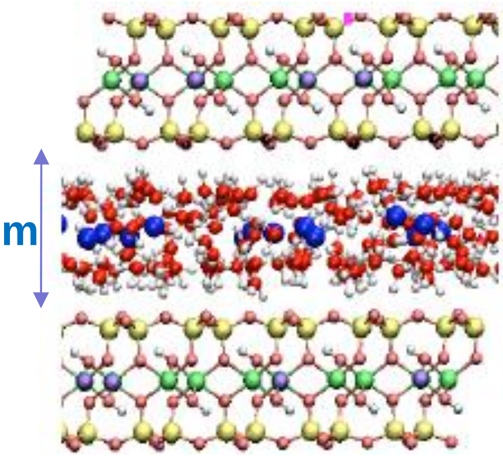
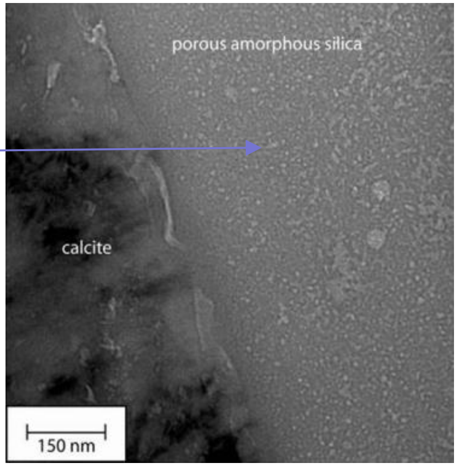
Nucleation in confinement



Cap rock:
clay minerals



Reservoir rock:
Sandstone



Daval et al.
Am. Min (2009)

- **Confinement induces a strong structuring of the fluid and restricted dynamics**

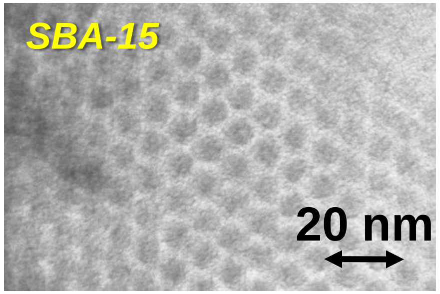
How does confinement affect nucleation barriers?

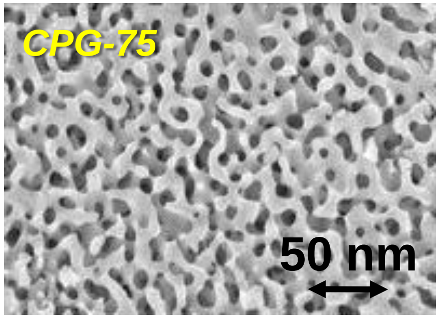
Nucleation in confinement

Synergistic experimental – modeling approach

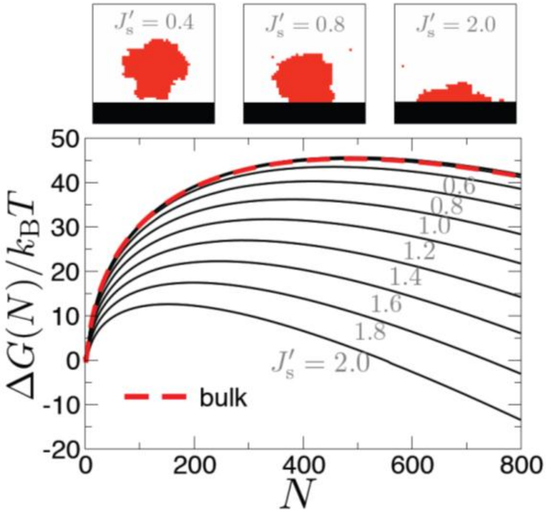
Mesoporous silica materials

Tunable pore sizes from 2 – 100 nm



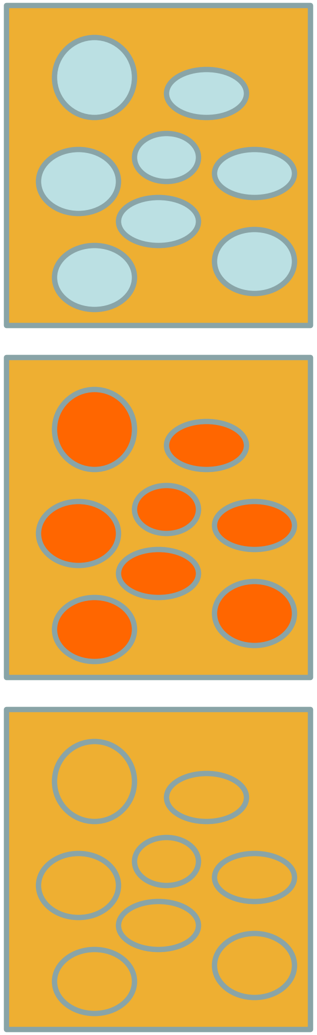


Statistical mechanics models

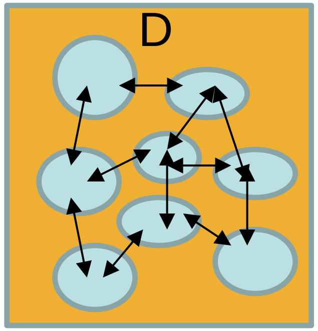


A synergistic experimental – modeling approach has been adopted to study the effect of confinement on carbonate mineral nucleation and growthin nanopores

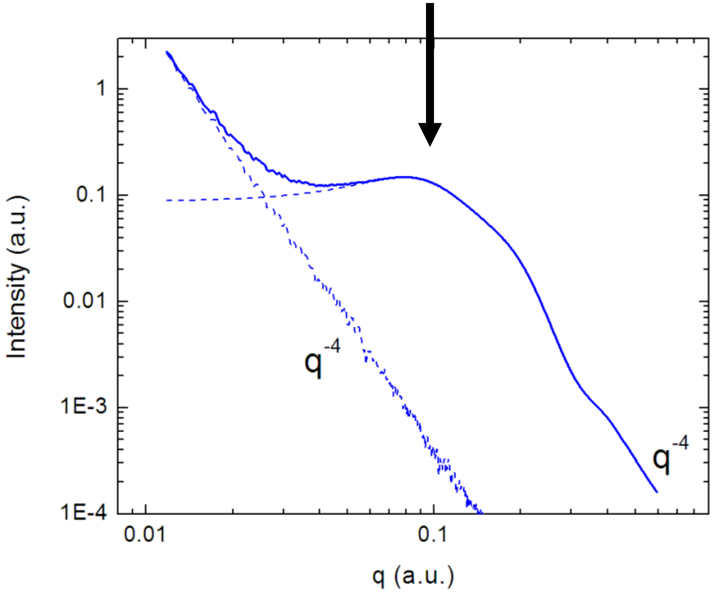
Nucleation in confinement: SAXS/SANS



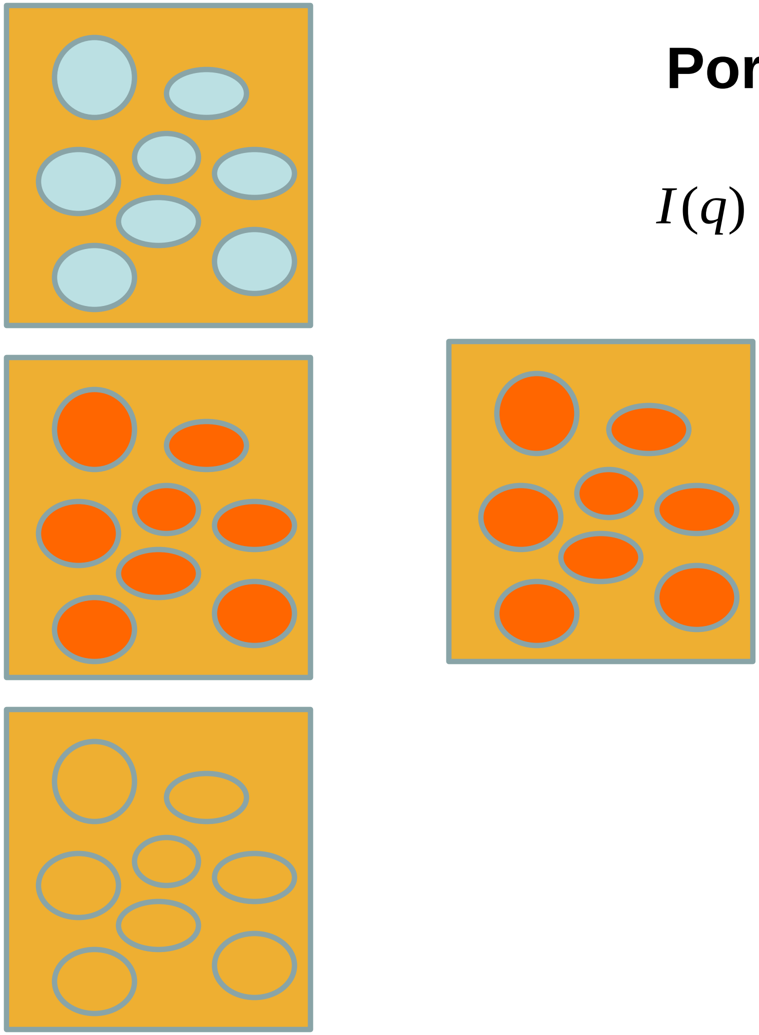
Pores filled with water



$D \sim 2\pi/q$

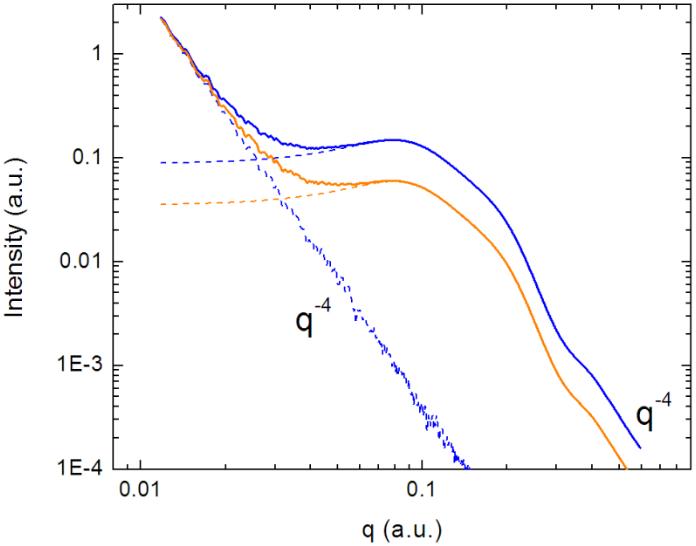


Nucleation in confinement: SAXS/SANS

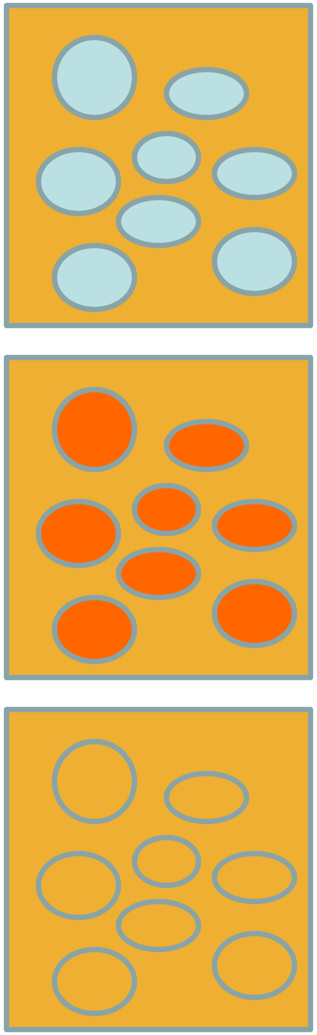


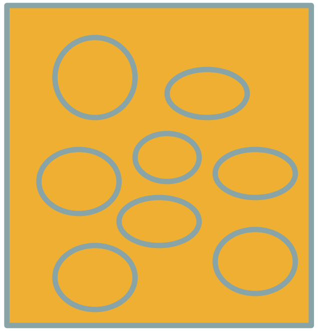
Pores filled with calcite

$$I(q) \approx NV^2 \boxed{(\rho_1 - \rho_2)^2} P(q)S(q)$$



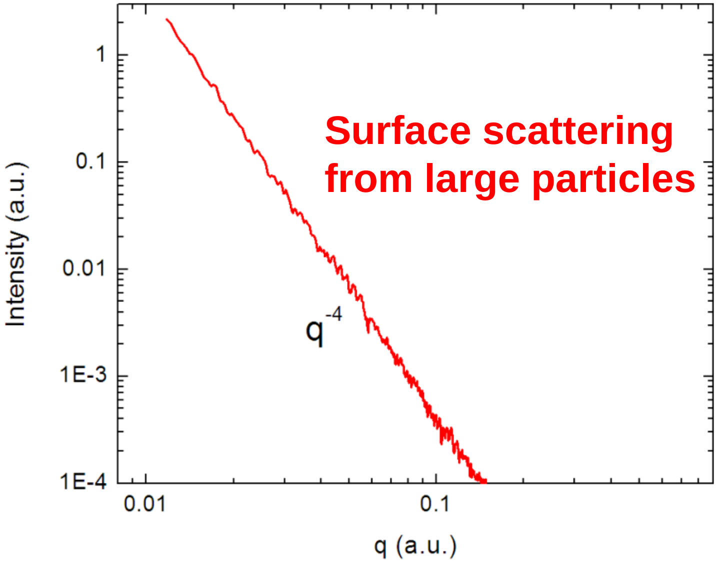
Nucleation in confinement: SAXS/SANS





No pores ⇒ $\rho_1 = \rho_2$

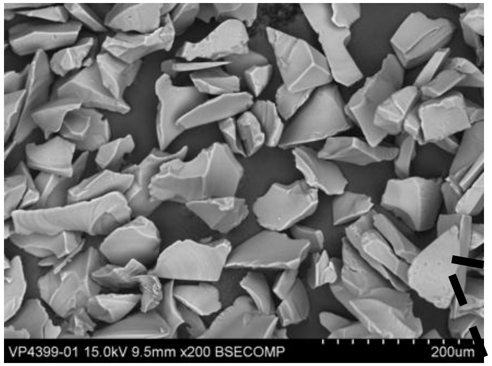
$$\cancel{I(q)} \approx NV^2(\cancel{\rho_1 - \rho_2})^2 P(q)S(q)$$



Surface scattering from large particles

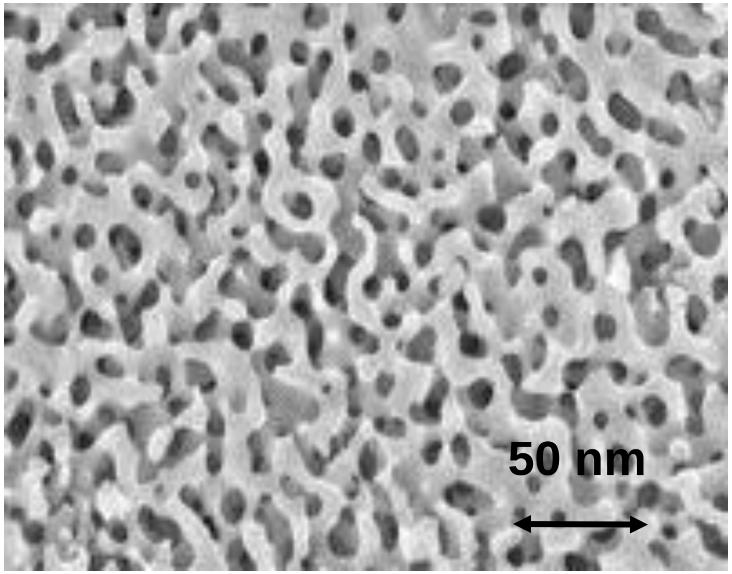
Neutron scattering contrast matching H_2O/D_2O

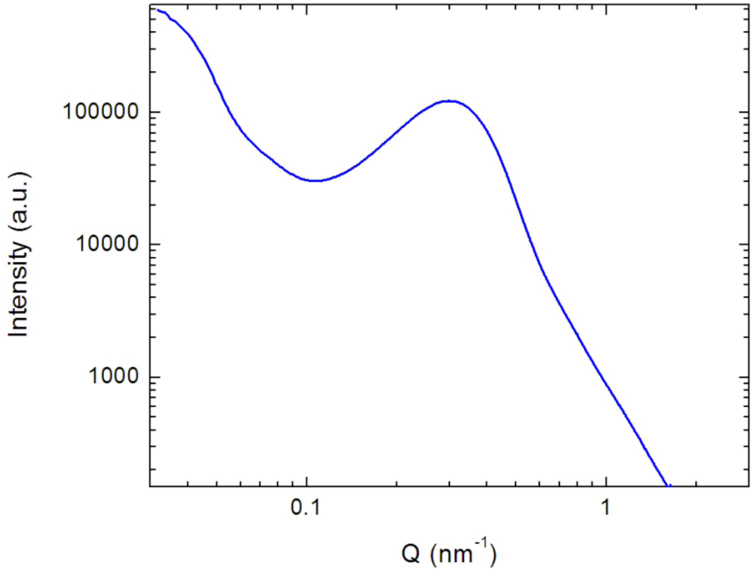
Nucleation in confinement: SAXS/SANS



Controlled Pore Glass-75

Controlled Pore Glass-350





Stack, Fernandez-Martinez, Rother, Waychunas, Cole

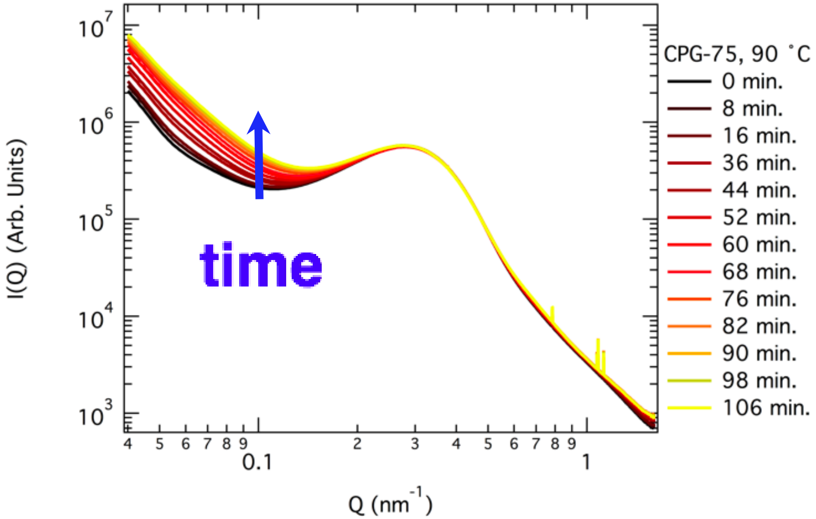
Nucleation in confinement: in situ SAXS

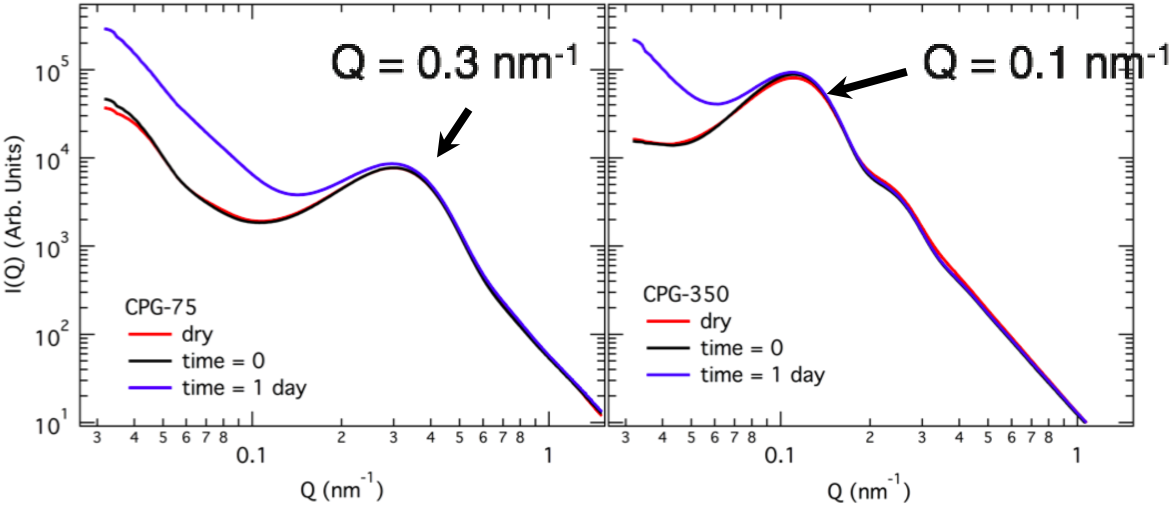
Pure CPG materials – SiO_2

σ = 1 $CaCO_3$ solution

T = 90°C

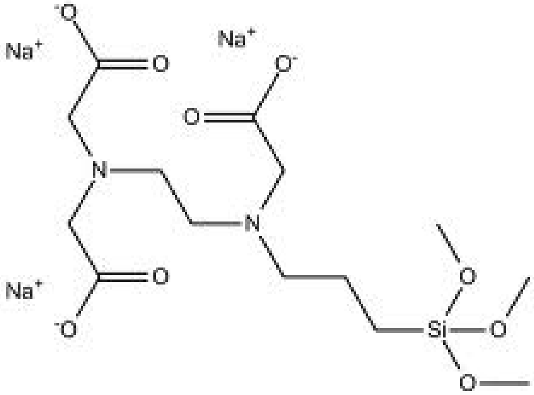
Precipitation in large pores





Nucleation in confinement: functionalization

functionalization



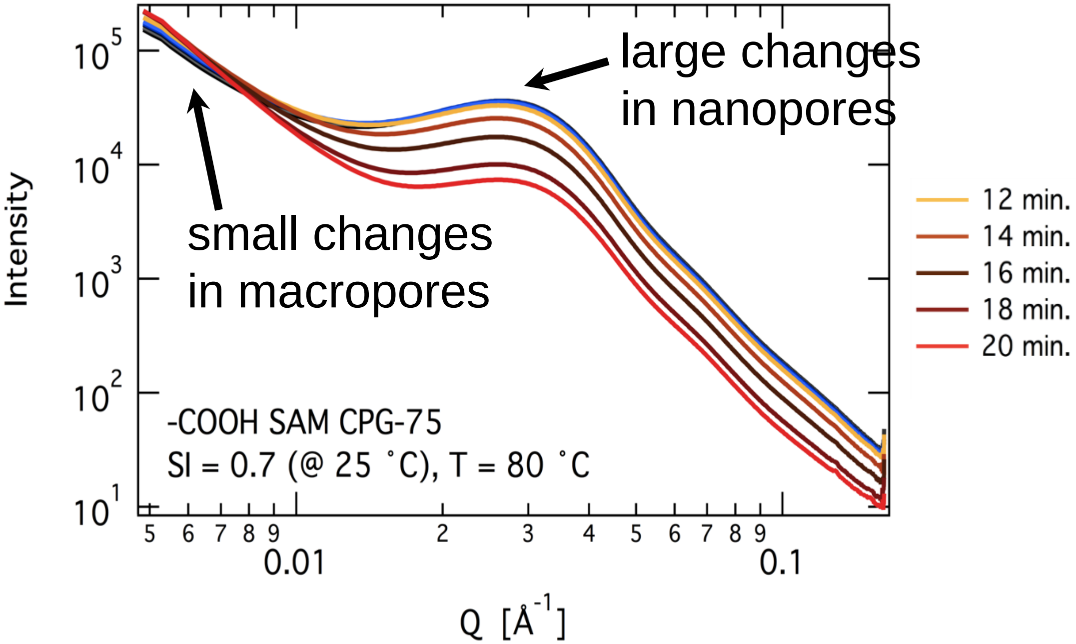
Nucleation in confinement: *in situ* SAXS

Functionalized CPG materials: carboxyl – terminated SiO_2

σ = 1 $CaCO_3$ solution

T = 90°C

Precipitation in nano pores



large changes in nanopores

small changes in macropores

Conclusions

- **$CaCO_3$ precipitation only in large pores (inter-grain) of pure SiO_2 porous materials**

- **$CaCO_3$ precipitation inside the nanopores after surface modification**

- **(Again) SAXS offers a unique capability to observe precipitation IN pores**

- **Confinement effects?**

In situ techniques

- **In situ experiments allow the determination of thermodynamic parameters such as interfacial free energies**

- **Scattering techniques probing nm-scale nuclei can give information about thermodynamics of nucleation**

Portable chemical reactor installed at beamline ID15 (ESRF) for in situ synchrotron experiments

- Control of pH, eH, titrations, stirring rate, pO2 and T
- Remotely controlled from the beamline hutch
- In situ High Energy X-ray Diffraction experiments and PDF analyses

Acknowledgements

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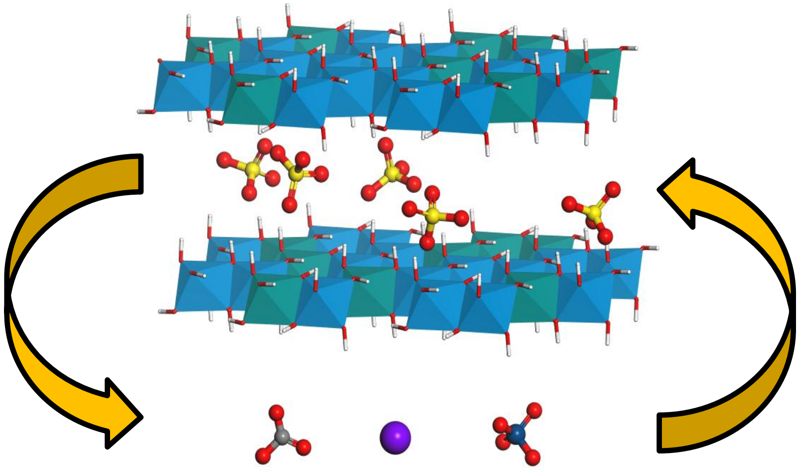
Andrew Stack
Gernot Rother
Leo Banuelos

OAK RIDGE National Laboratory

Yandi Hu
Jessica Ray
Young-Shin Jun

Washington University in St. Louis
SCHOOL OF ENGINEERING & APPLIED SCIENCE

See poster:
Échange Anionique de Radionucléides dans des Phases Cimentaires Sulfatés



$Ca_4Al_2(OH)_{12}\cdot X \cdot(2-6)H_2O$

$X = SO_4^{2-}, 2I^-, CO_3^{2-}, SeO_4^{2-}$