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HELMHOLTZ GEMEINSCHAFT

In situ and real time methods for mineral synthesis and characterization

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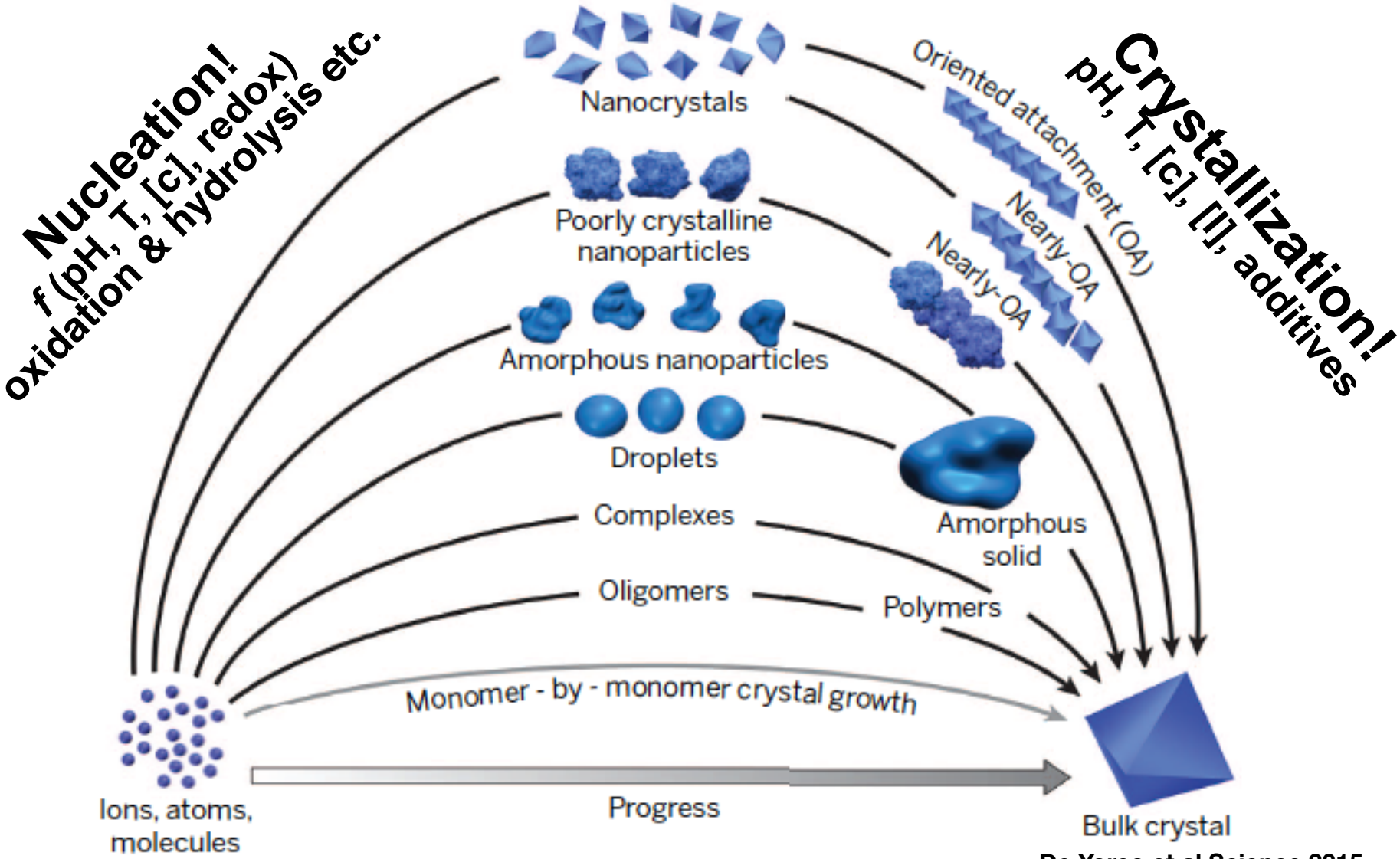
UNIVERSITY OF LEEDS

Atoms/Ions ➔ Nanoparticles ➔ Crystals
Kinetics *vs.* Thermodynamics!

- **Why** do / should we care ?
- **What** are we after?
- **How** do we do it?
- **How** can we overcome the limitations?

What does theory tell us!



De Yoreo et al Science 2015

The nanoscale dream *vs.* reality!

What data we want:

- atomic resolution
- size, shape, crystalinity
- all elemental speciation and distributions
- rates, mechanisms, energetics etc…
- *in situ* + realtime
- samples in an as ‘natural’ state as possible

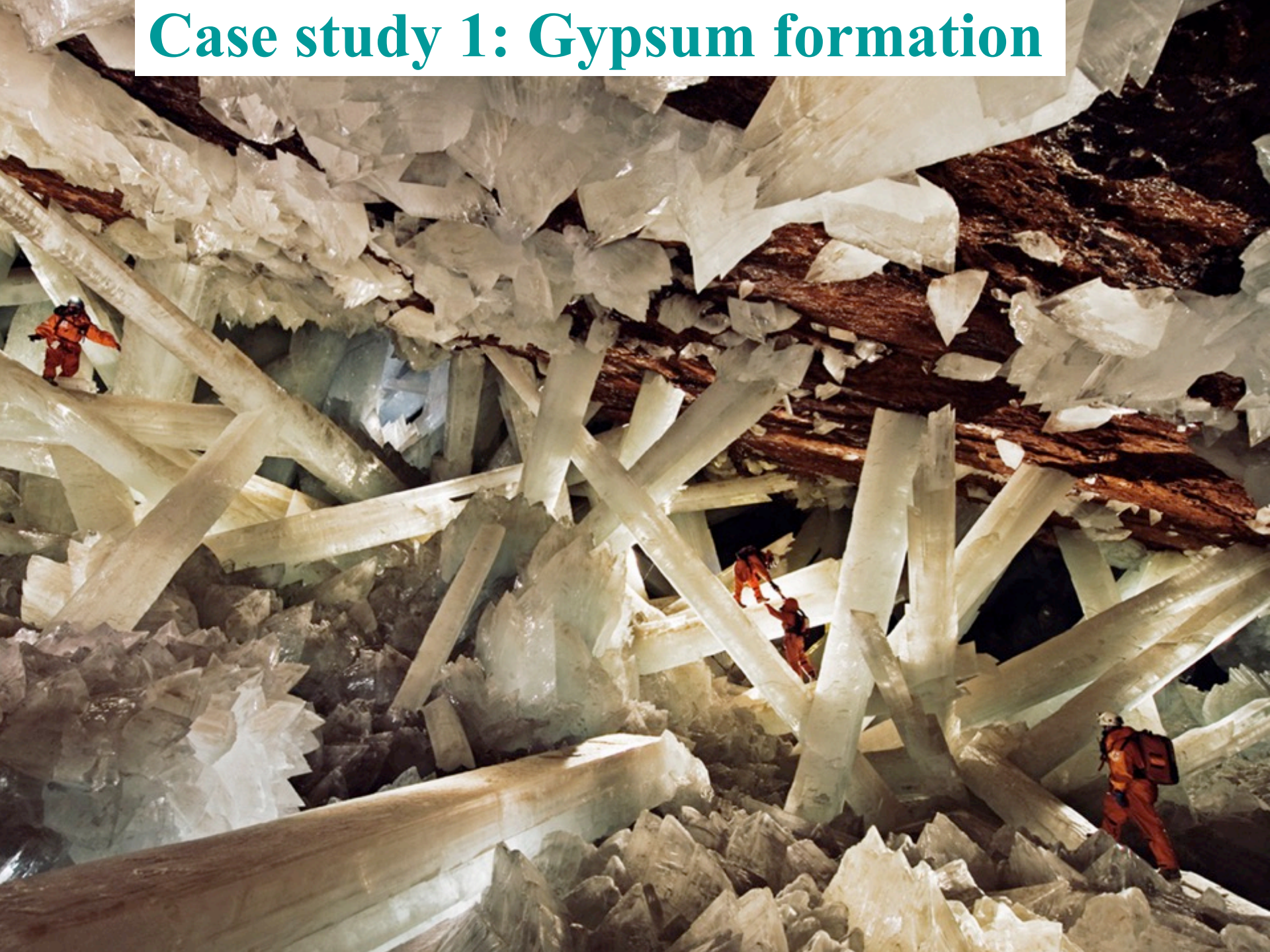
The good, the bad and the not so nice!

What we (think / hope we) can do !

- atomic resolution
- least X-ray or electron beam damage possible
- sample environment
    - vacuum / FIB sections / deposited on grids ….

      vs. as in situ as possible – e.g., cryo-sections / 'wet' ….
- multi – method approach = cross-confirmation
- the needle in the haystack problem !!

Case study 1: Gypsum formation



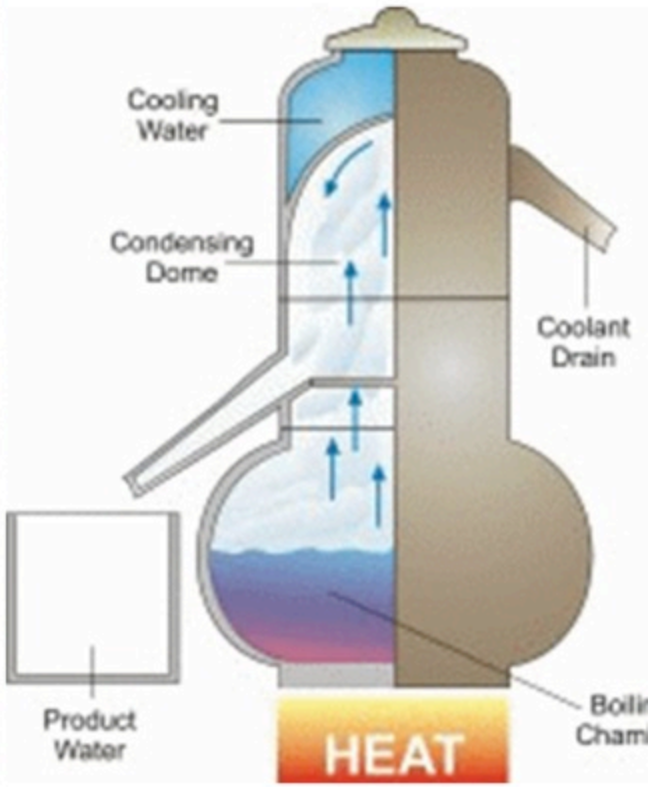
$CaSO_4$ …why?

Gypsum + heat ➔ Bassanite = Plaster of Paris

$$CaSO_4 \cdot 2H_2O + >> \text{energy} \rightarrow CaSO_4 \cdot 0.5H_2O$$

> 100 Mio tonnes / year

An important resource BUT…
Can we make it more efficient?
Can we Plaster the world cheaper?



2012 was the year of making Gypsum !

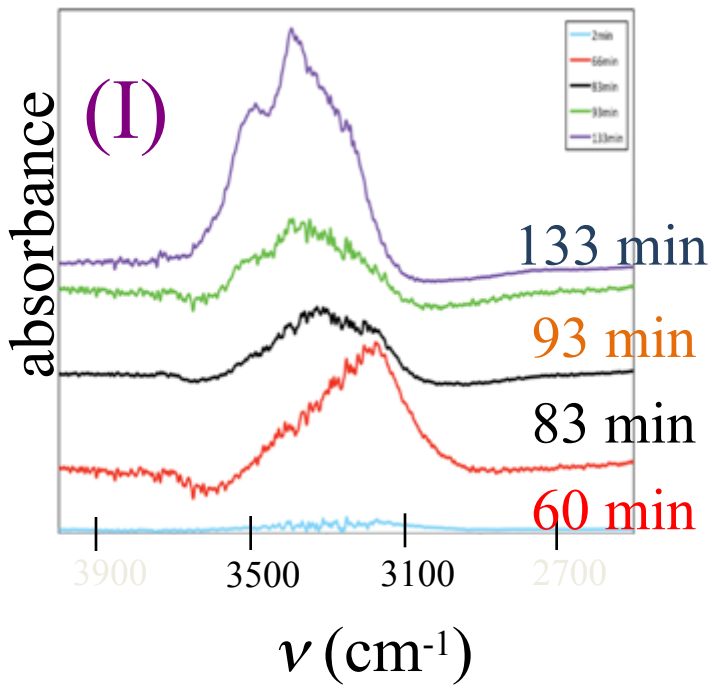
Solution

(I)

Amorphous $CaSO_4$

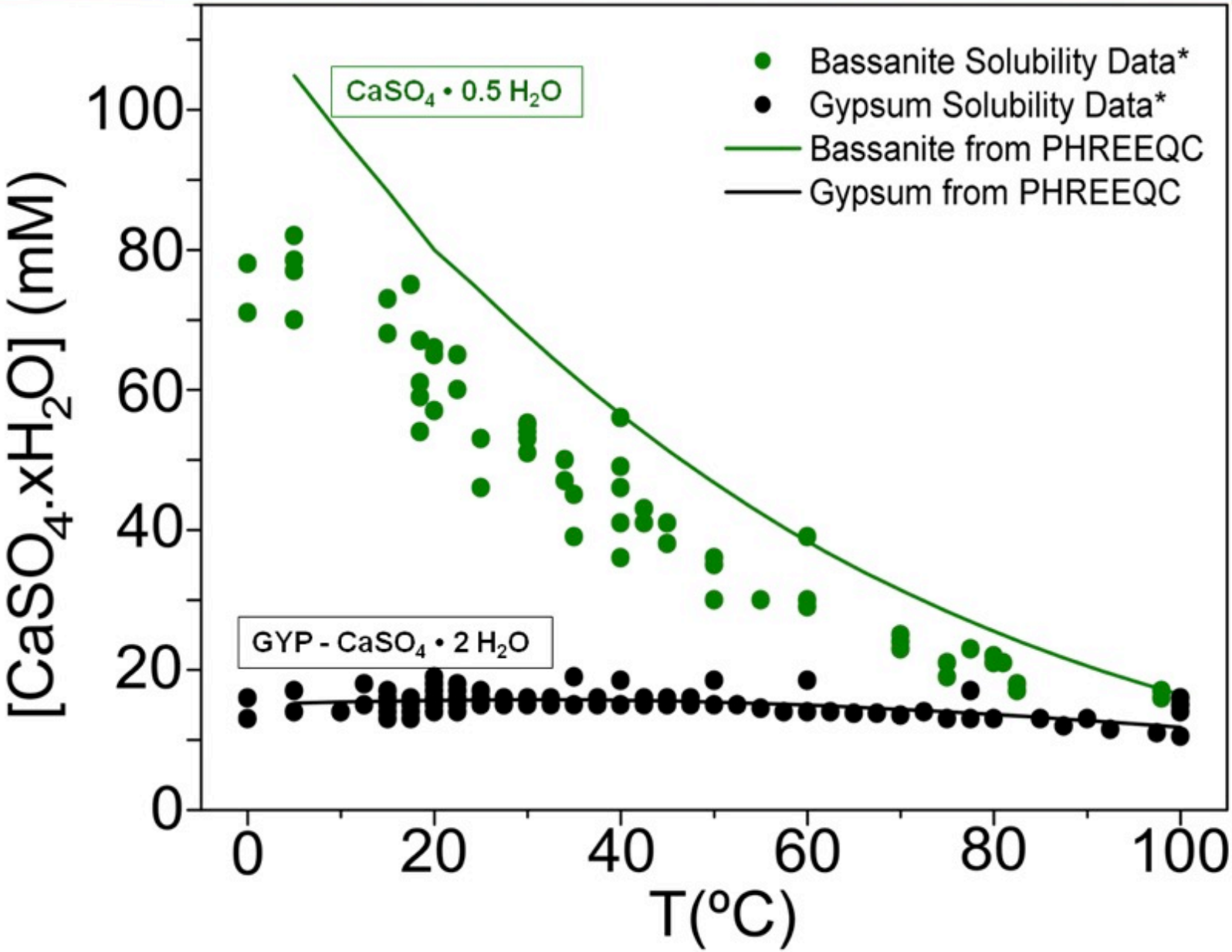
(I)

Gypsum ($CaSO_4 \cdot 2H_2O$)



(I) Jones *CrystEngComm. Eng.* (2012)

What does thermodynamics tell us?



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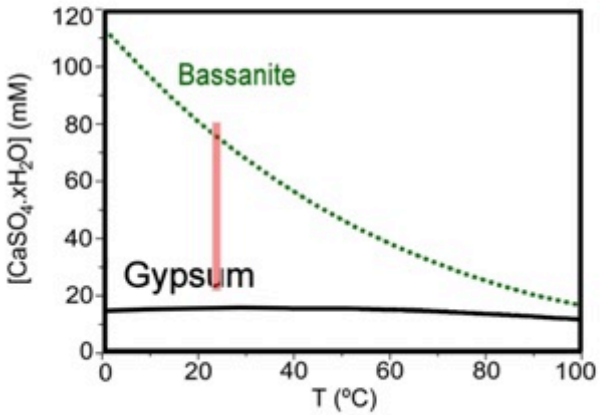
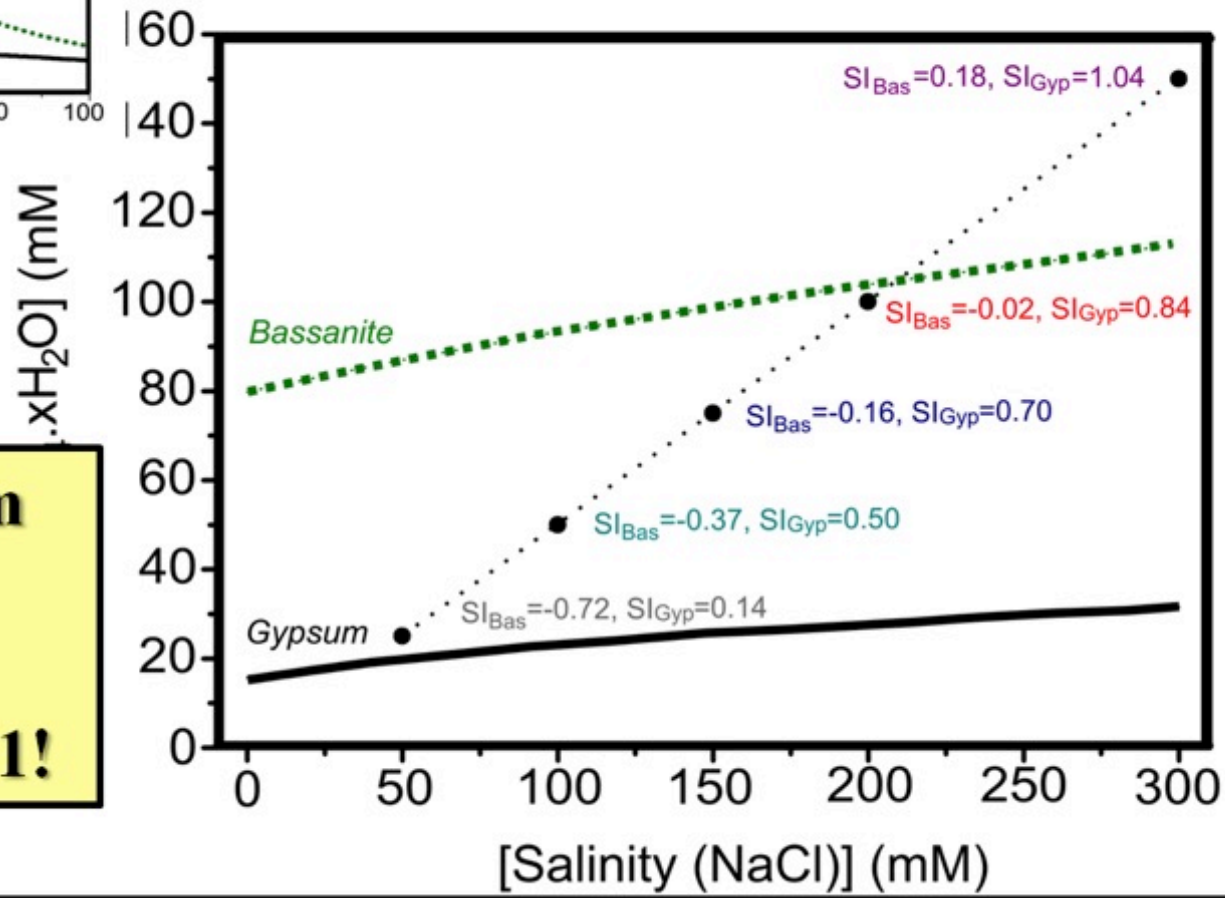
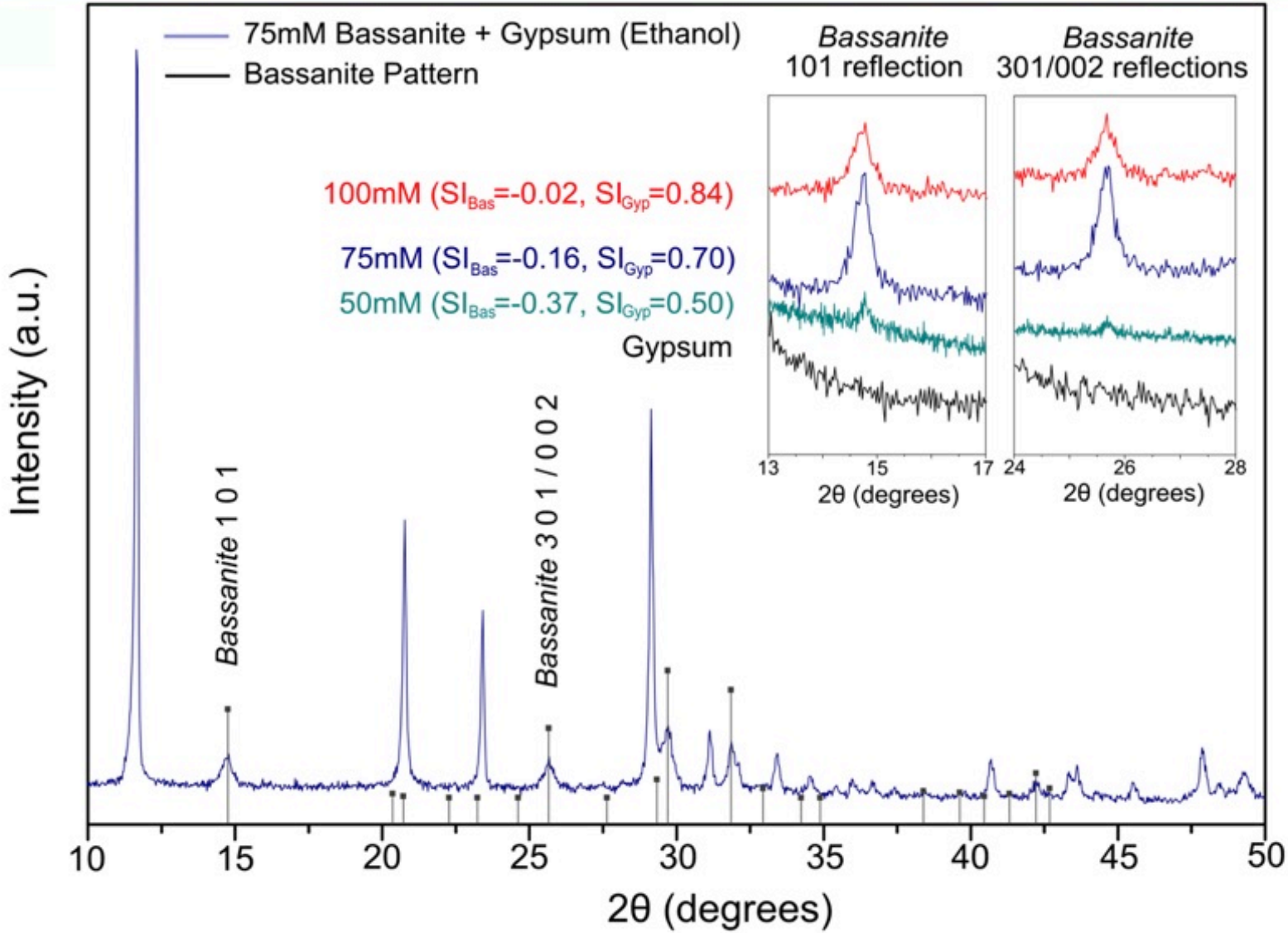


$CaSO_4$ solution ➔ ACS ➔ Gypsum ➔Bassanite

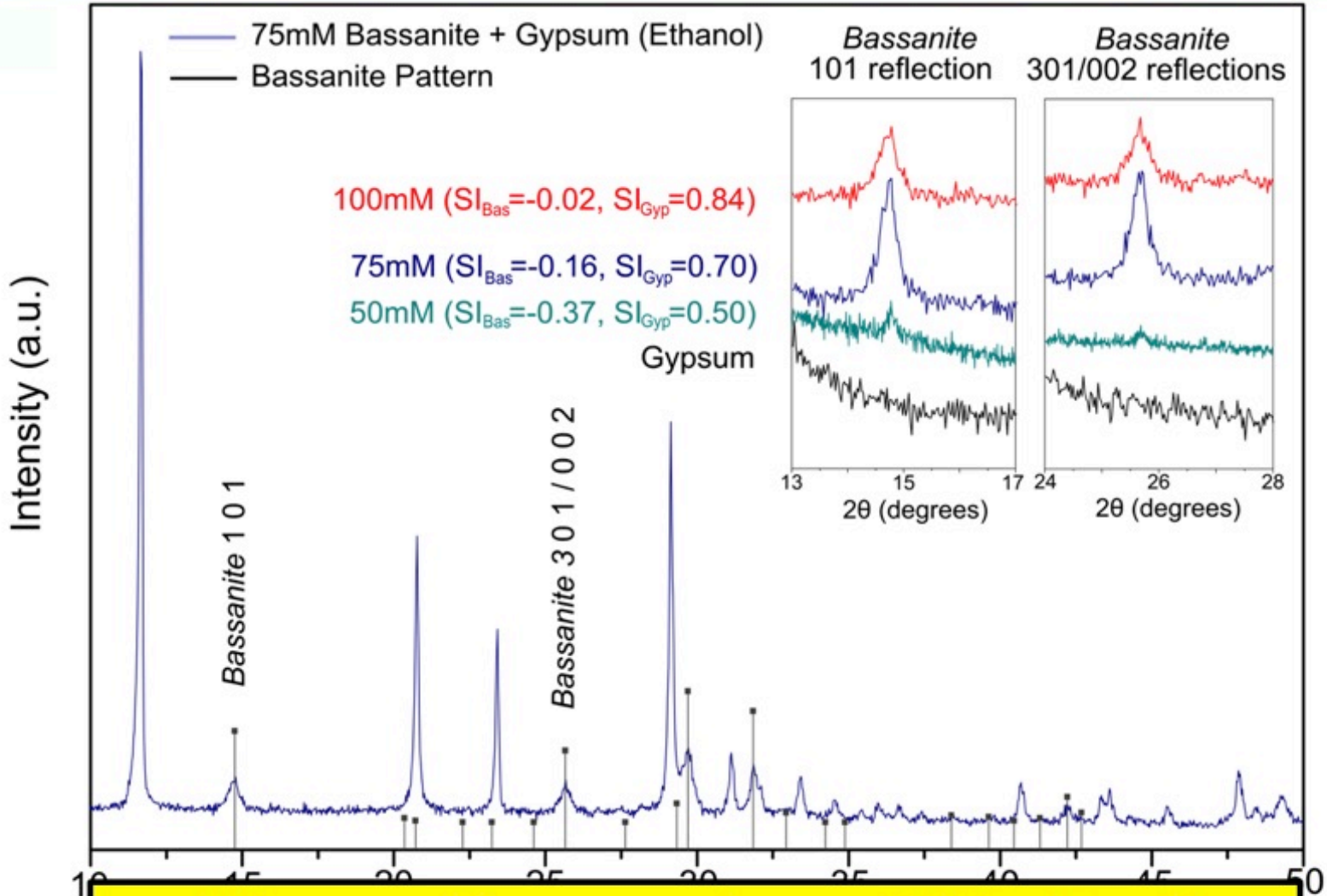


Only Gypsum should precipitate below SI_{Gyp} = 1!

When a supervisor doubts a student!

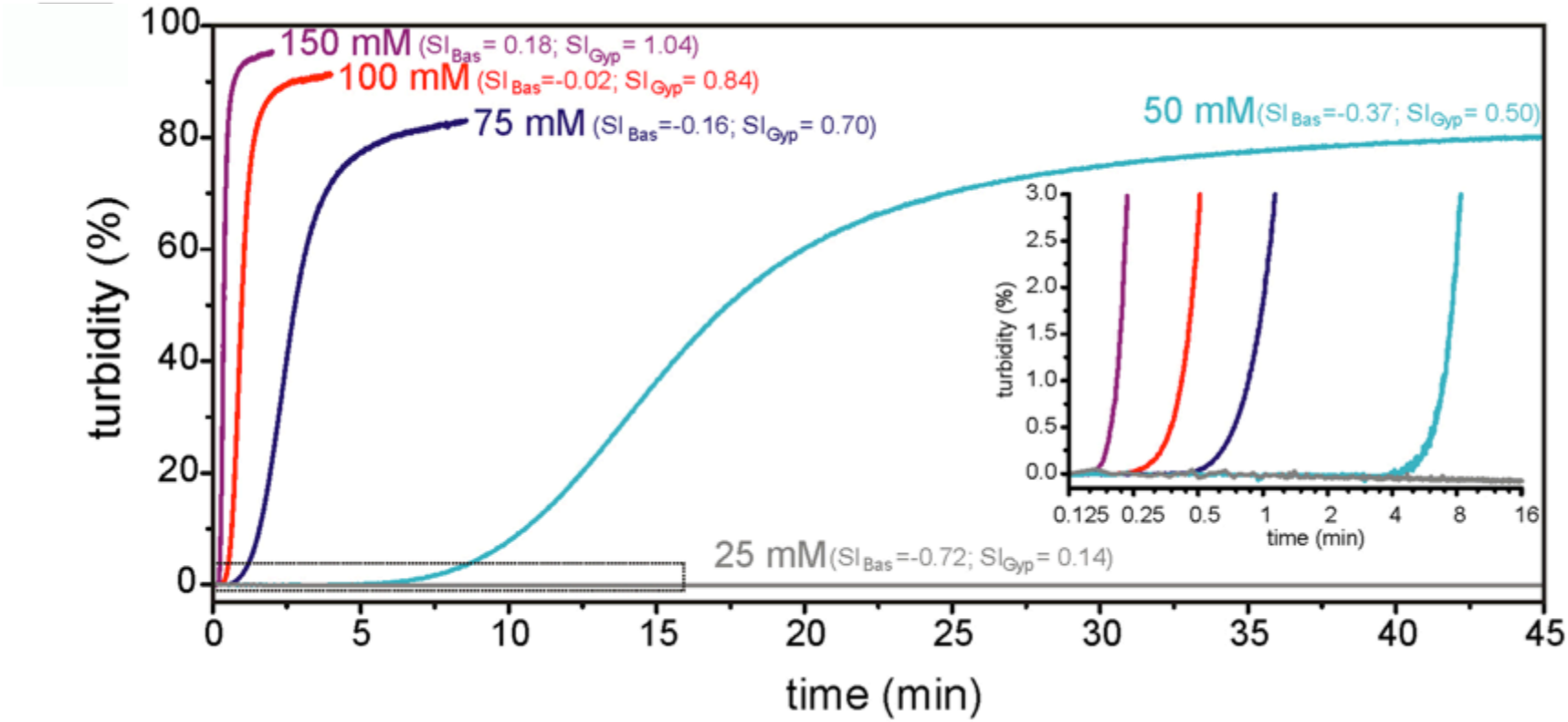


When a supervisor doubts a student!



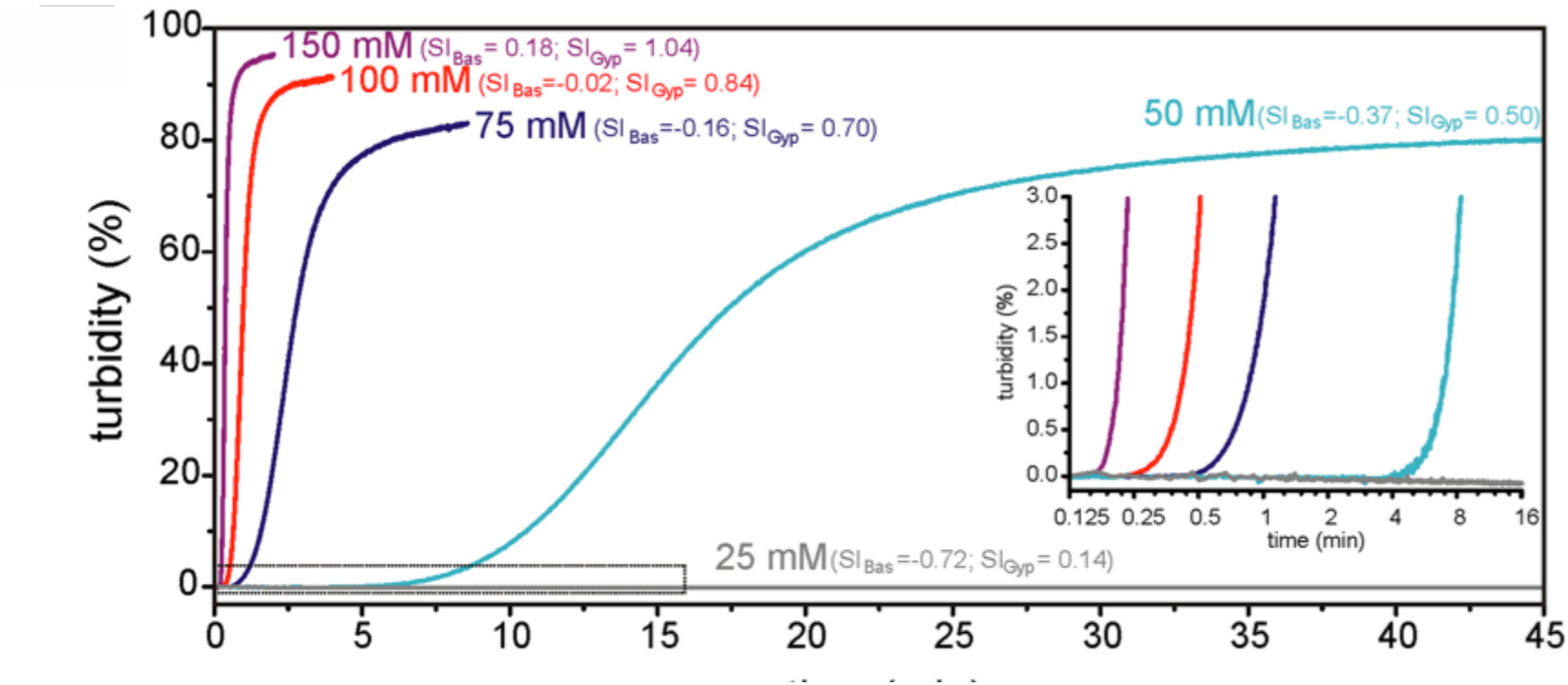
The case of a supervisor not listening !!

So let us prove it!



Van Driessche et al Science 2012

So let us prove it!



Need a fast and high spatial and temporal resolution approach!

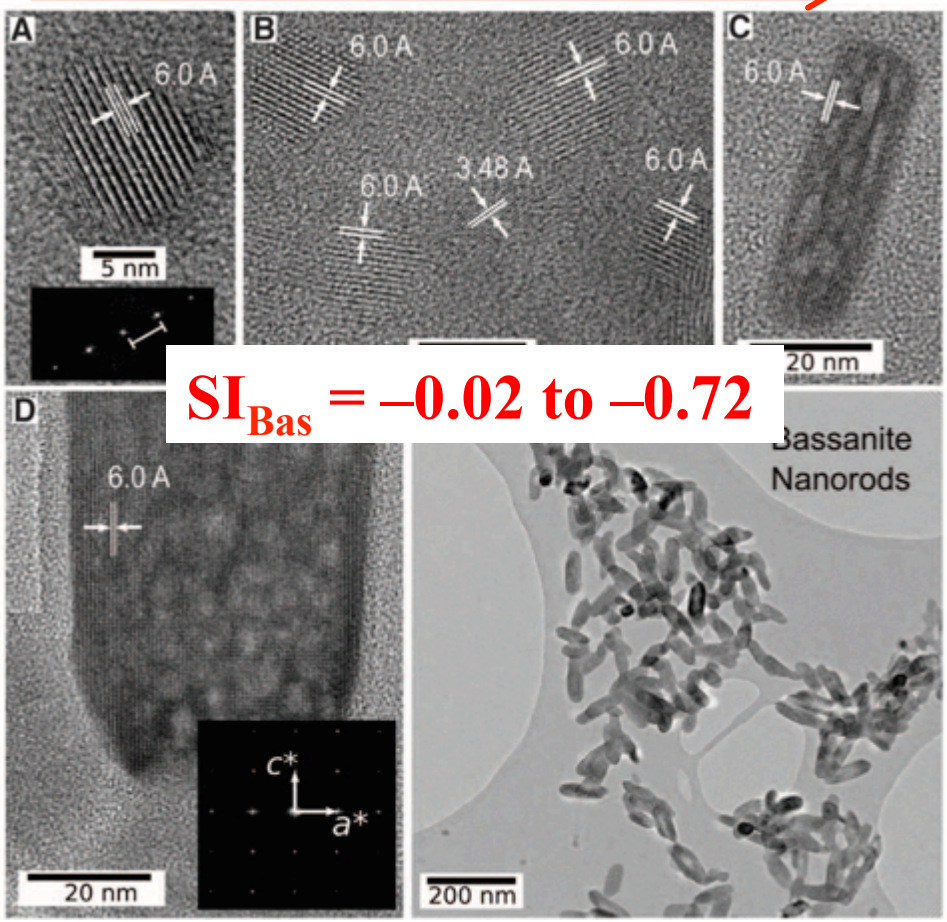
…that does not suffer from *too many* artefacts!

Van Driessche et al Science 2012

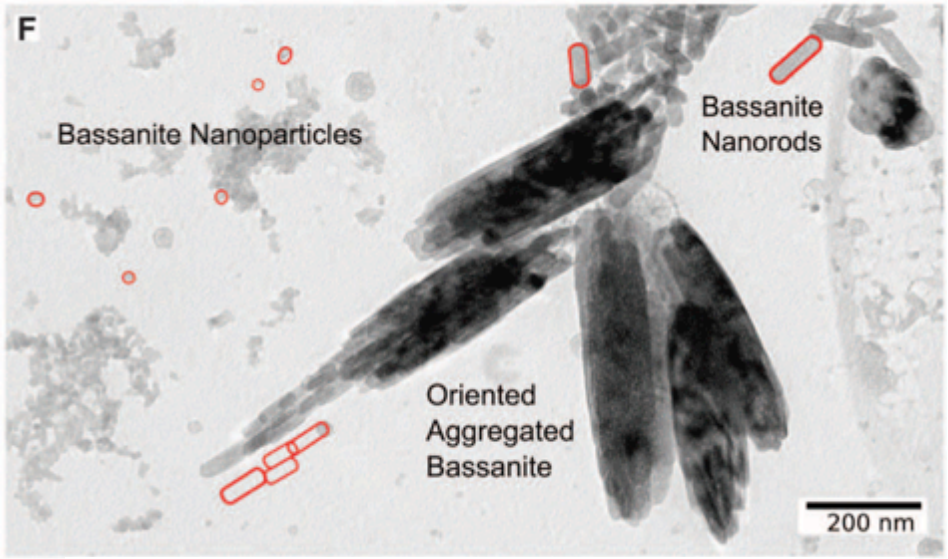
HR-TEM ± cryo-options

Cryo-quench and cryo- / HR-TEM

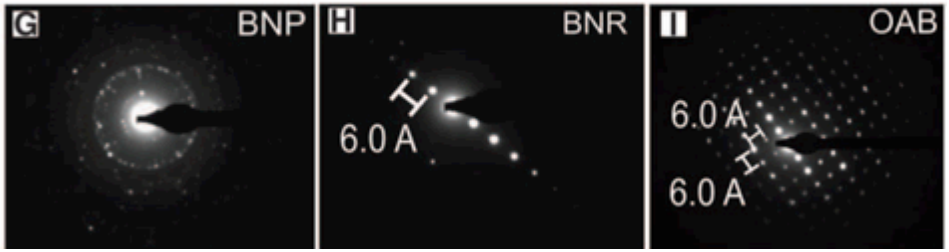
Time



SI_{Bas} = –0.02 to –0.72

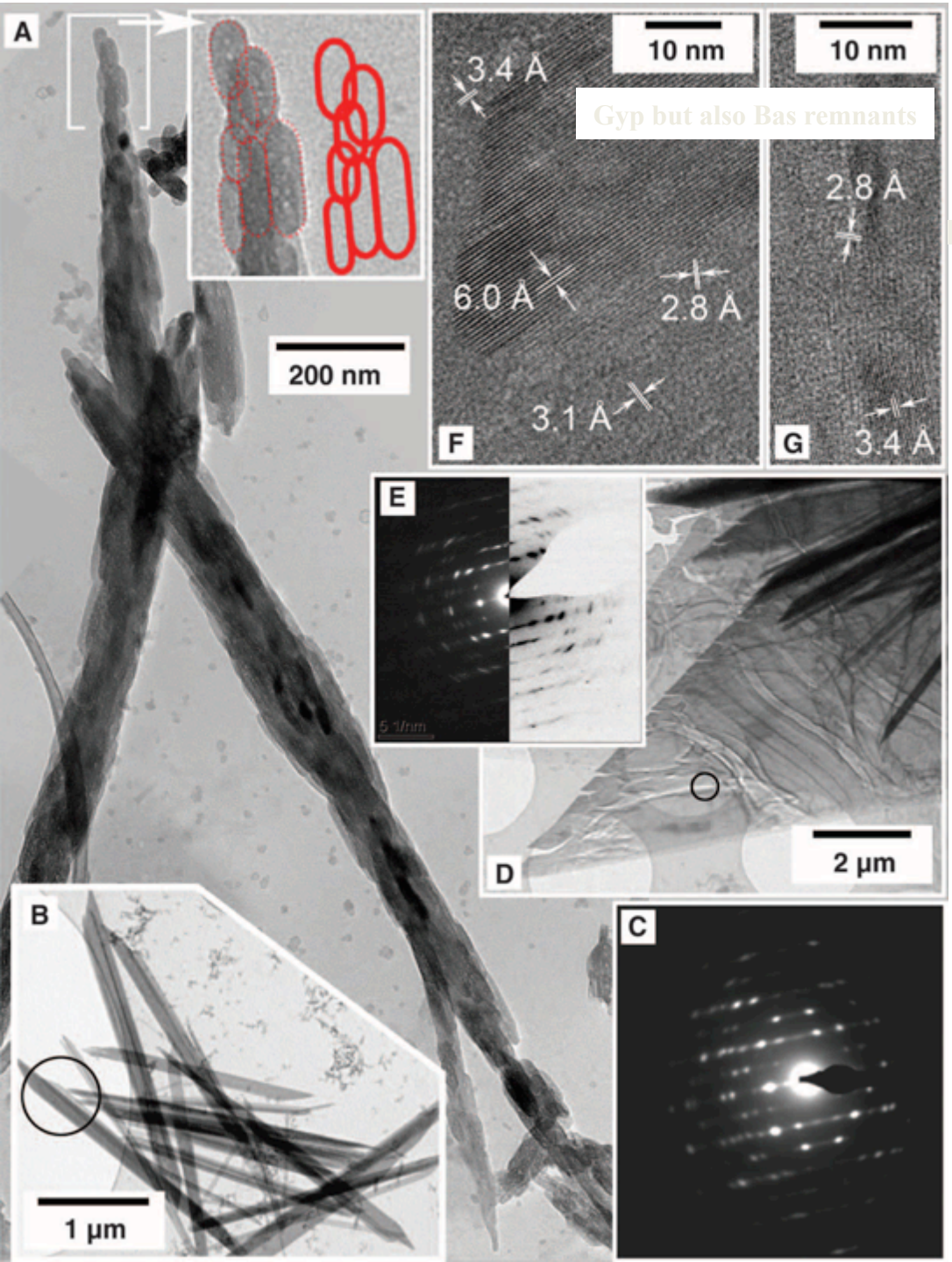


Solubility of Bas_{Nano} < Bas_{Bulk}



Bassanite ($CaSO_4 \cdot 0.5H_2O$) forms from solution as nanocrystals

NO ACS NO direct Gypsum !!



Bassanite ➔ Gypsum?

- **Oriented self-assembly of Bas nanorods and recrystallization to Gyp**

<u>What does this mean?</u>

- Bas_{Nano} formed at $SI_{Bas} < 1$
- Bas_{Nano} formed < solubility of Bas_{Bulk} and solubility of Gyp
- classical dehydration / crystallization pathway not followed as Bas = 0.5 H_2O and Gyp = 2 H_2O
- nano-crystals to macro-crystals

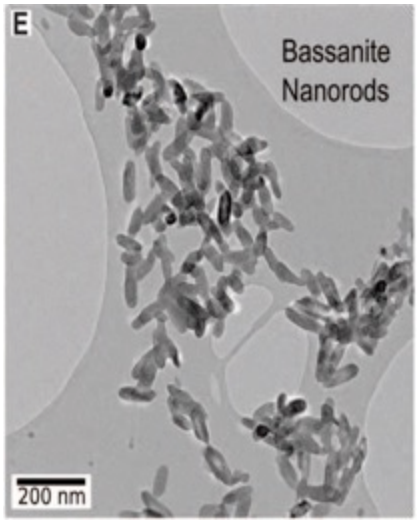
Van Driessche et al Science 2012

2012 was the year of making Gypsum !

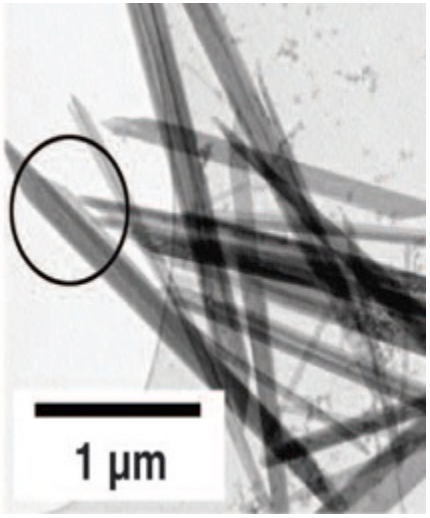
Solution $\xrightarrow{(II)}$ **Bassanite ($CaSO_4 \cdot 0.5H_2O$)**

$\downarrow$ (II)

Gypsum ($CaSO_4 \cdot 2H_2O$)



(II) $\rightarrow$



(II) Van Driessche et al., *Science* (2012)

2012 was the year of making Gypsum !

Solution

↓

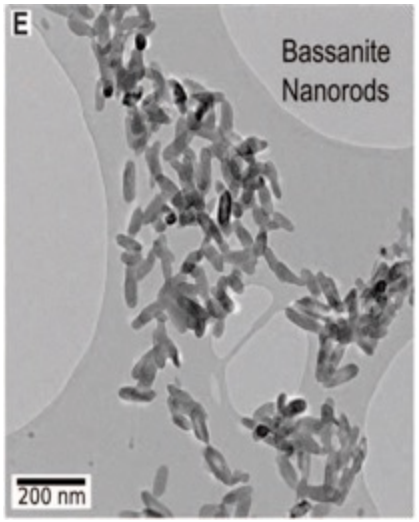
Amorphous $CaSO_4$

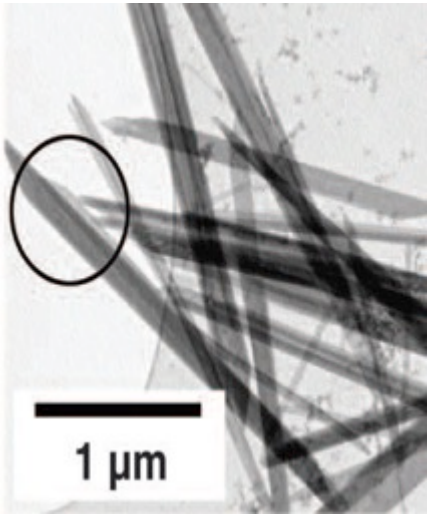
(III) →

Bassanite ($CaSO_4 \cdot 0.5H_2O$)

↓

Gypsum ($CaSO_4 \cdot 2H_2O$)



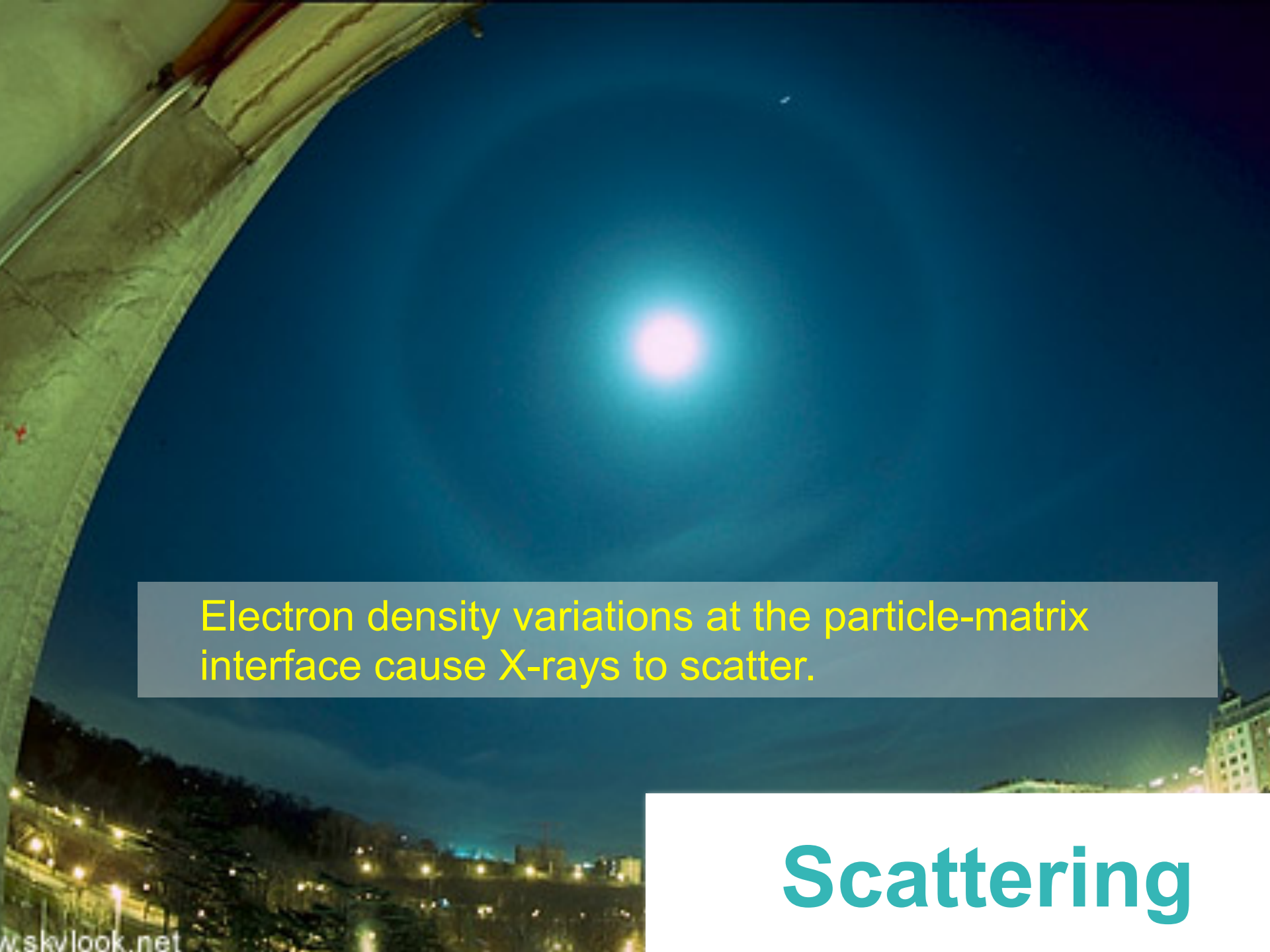


(III) Wang et al., *Chem. Commun.* (2012)

2012 was the year of making Gypsum !

What is real and what is an artefact?

***in situ vs.* ex situ!**



Electron density variations at the particle-matrix interface cause X-rays to scatter.

Scattering

What can we get from SAXS / WAXS?

SAXS

- Particle size
- Particle shape (structure, roughness)
- Polydispersity
- Aggregation mode

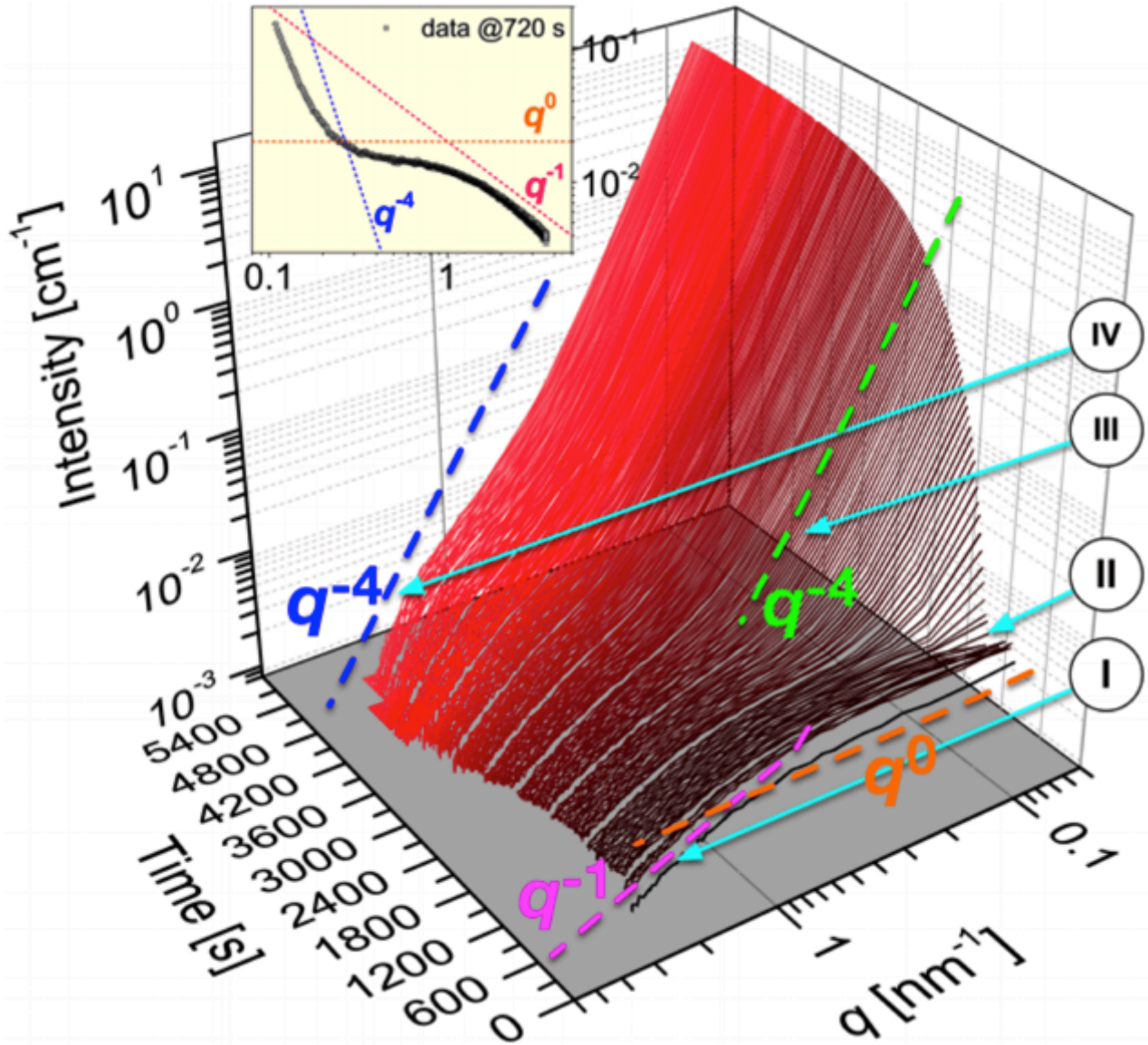
WAXS ≈ PXRD but in solution and fast

- Phase identification
- Crystallinity

From time resolved SAXS + WAXS

- Kinetics
- Mechanisms
- Energetics
- Combined with complementary data – full picture

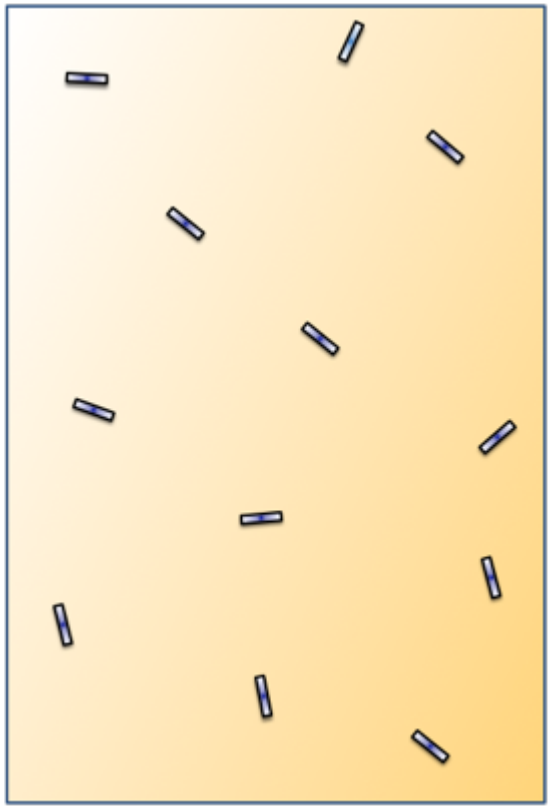
In situ and time resolved SAXS

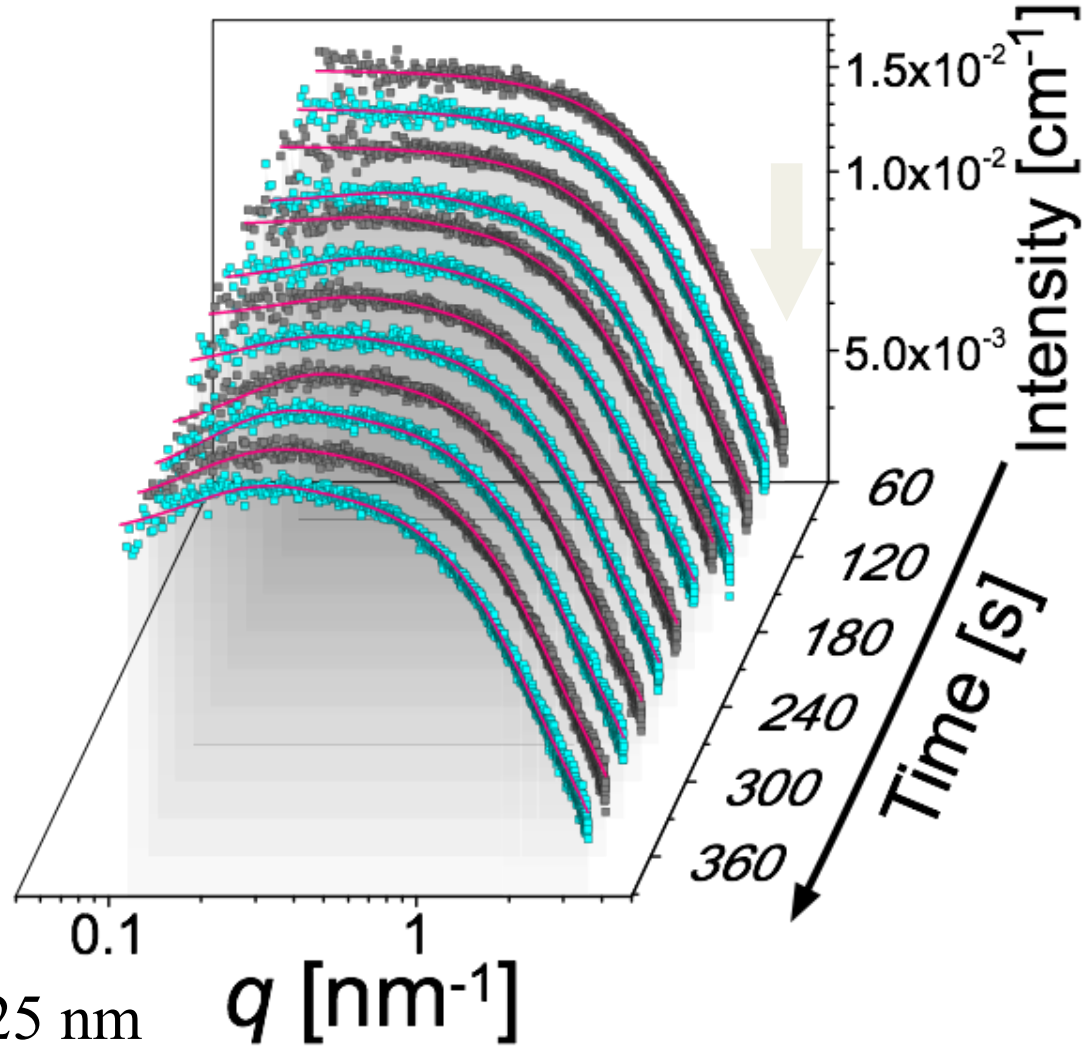


* Stawski et al., *Nature Com*. 7 (2016) 1177

Formation of elongated nano-units

➡ **Stage** Ⓘ



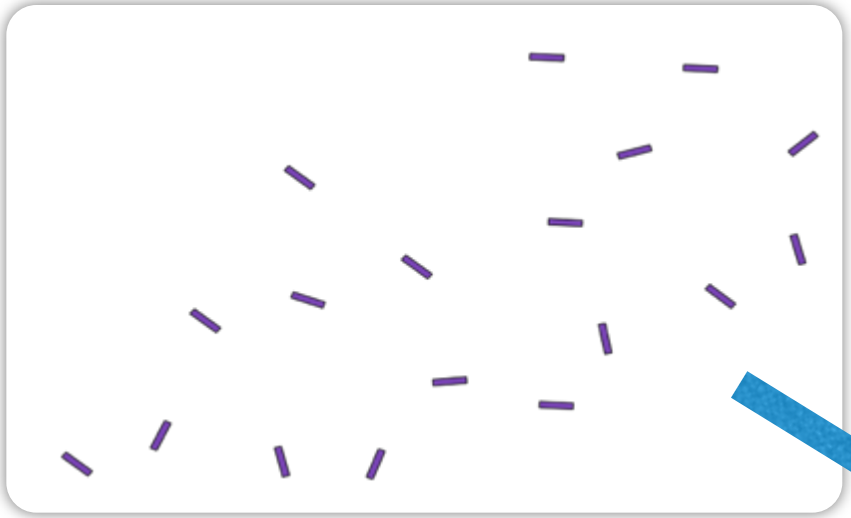


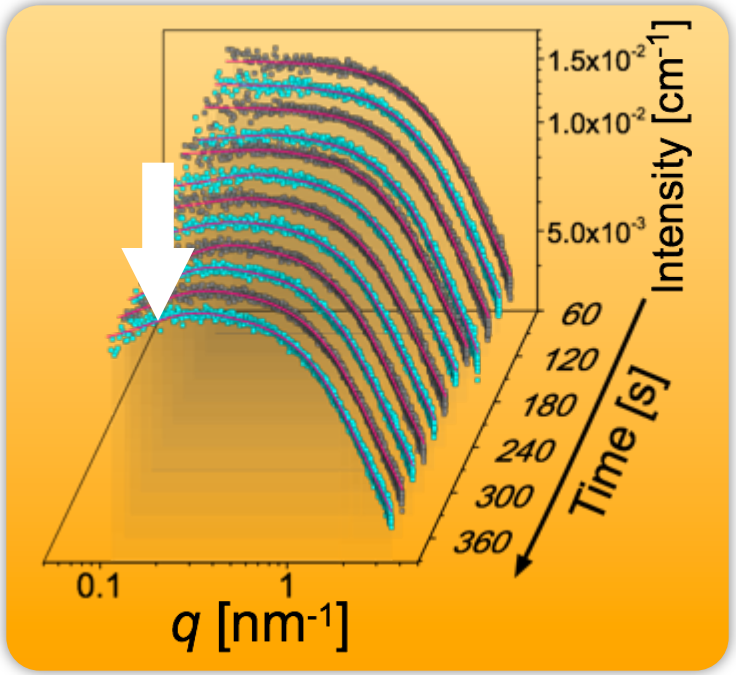
$L \approx$ 2.5 - 4 nm

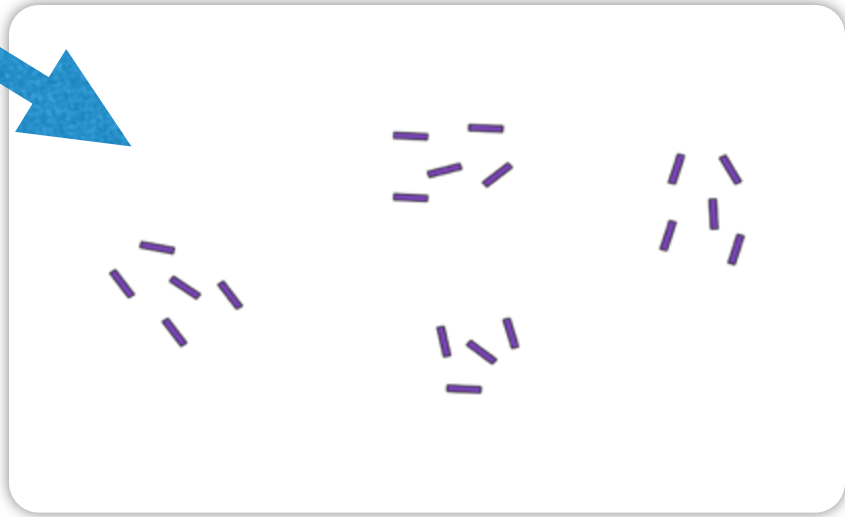
$d \approx$ 0.25 nm

Structure factor and aggregation

➡ **Stages** Ⓘ & Ⓘⓘ





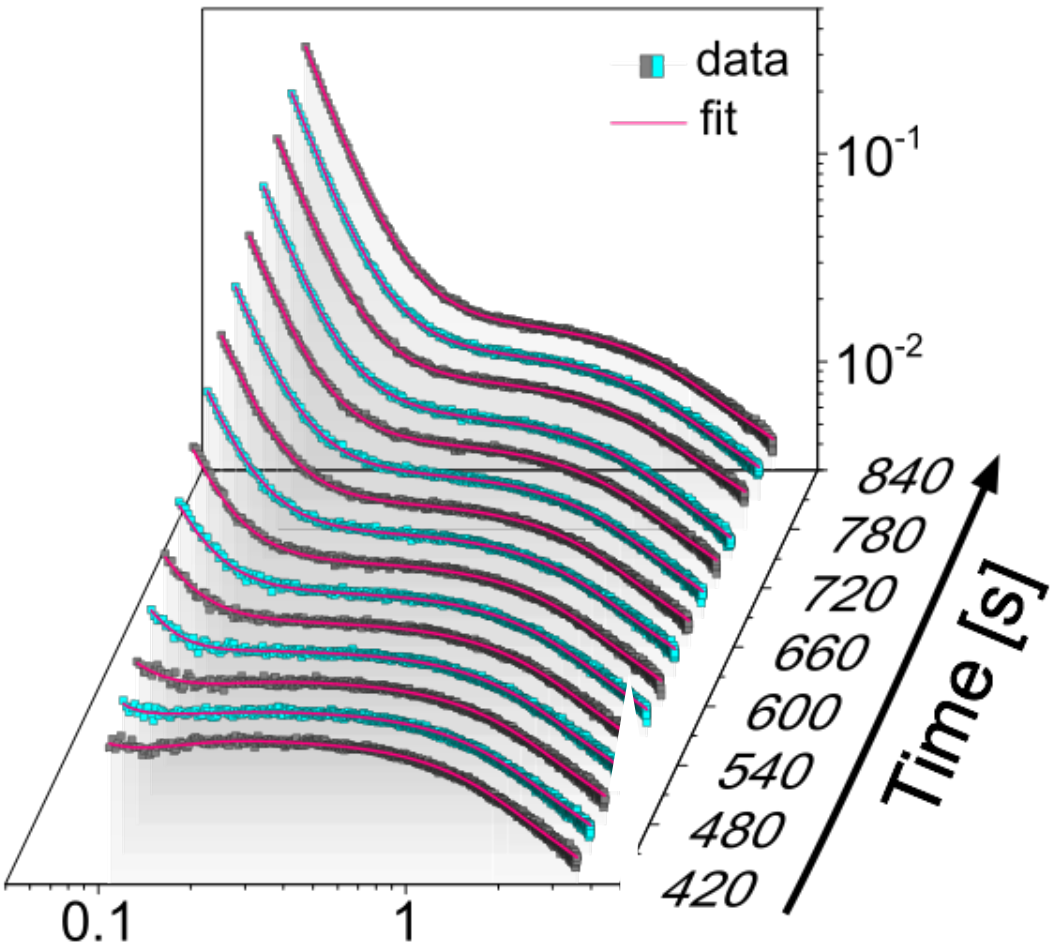


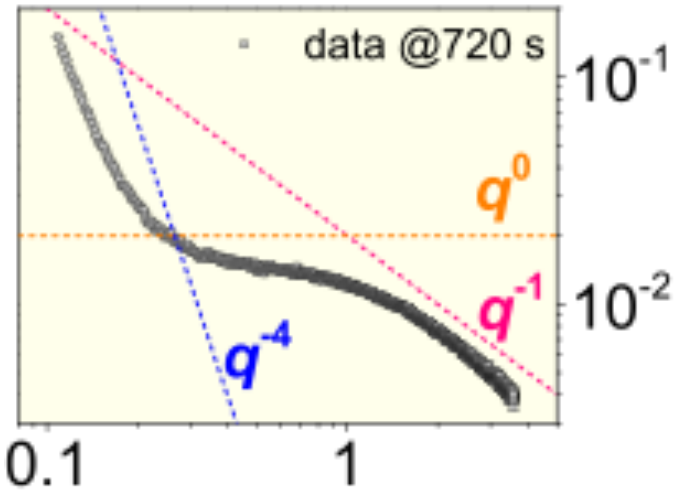
$L \approx$ 2.5 - 4 nm

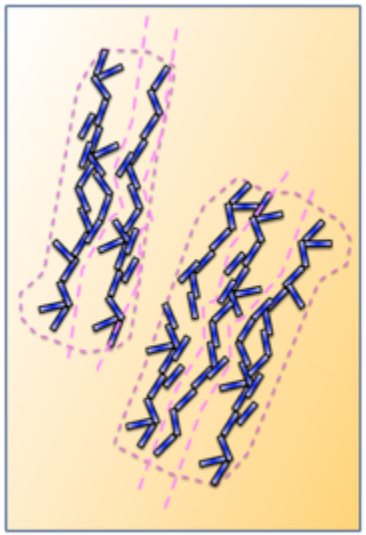
$d \approx$ 0.25 nm

Surface fractals + larger units

➡ **Stage III**

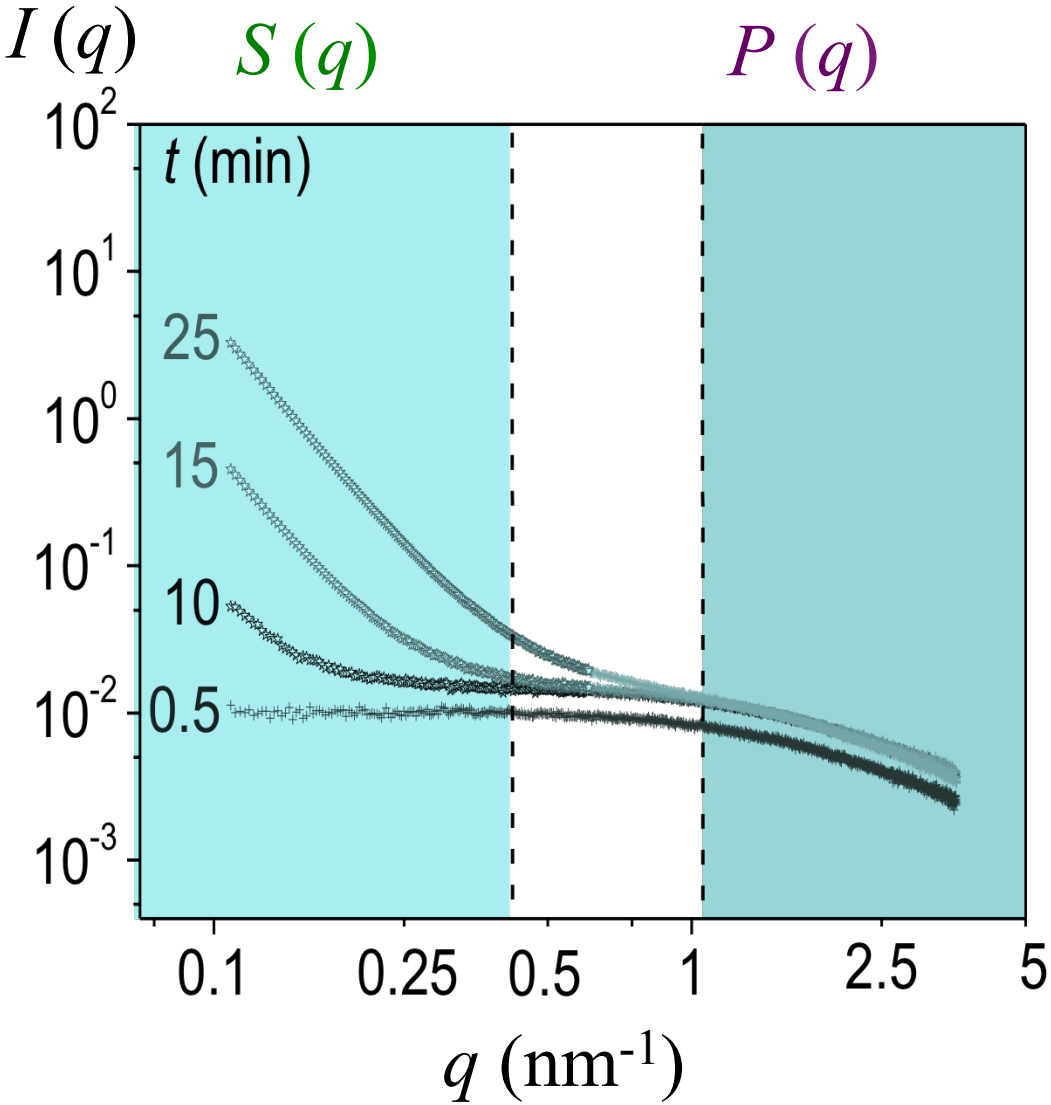






No change in P(q)

SAXS: elongated bricks → "Brick-in-a-wall"

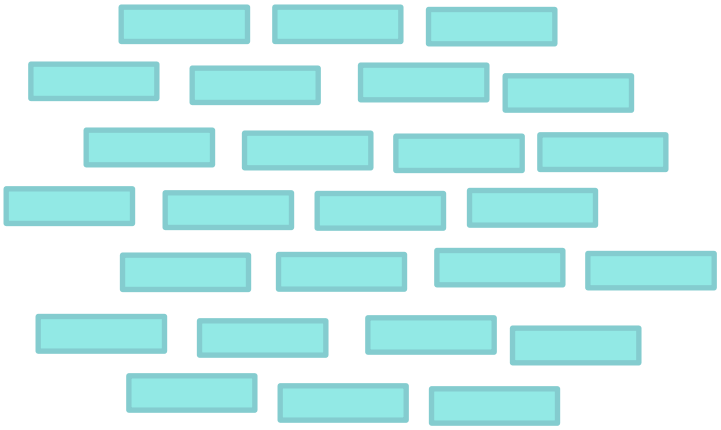


$P(q)$: Form factor

$L \approx$ 2.5 - 4 nm

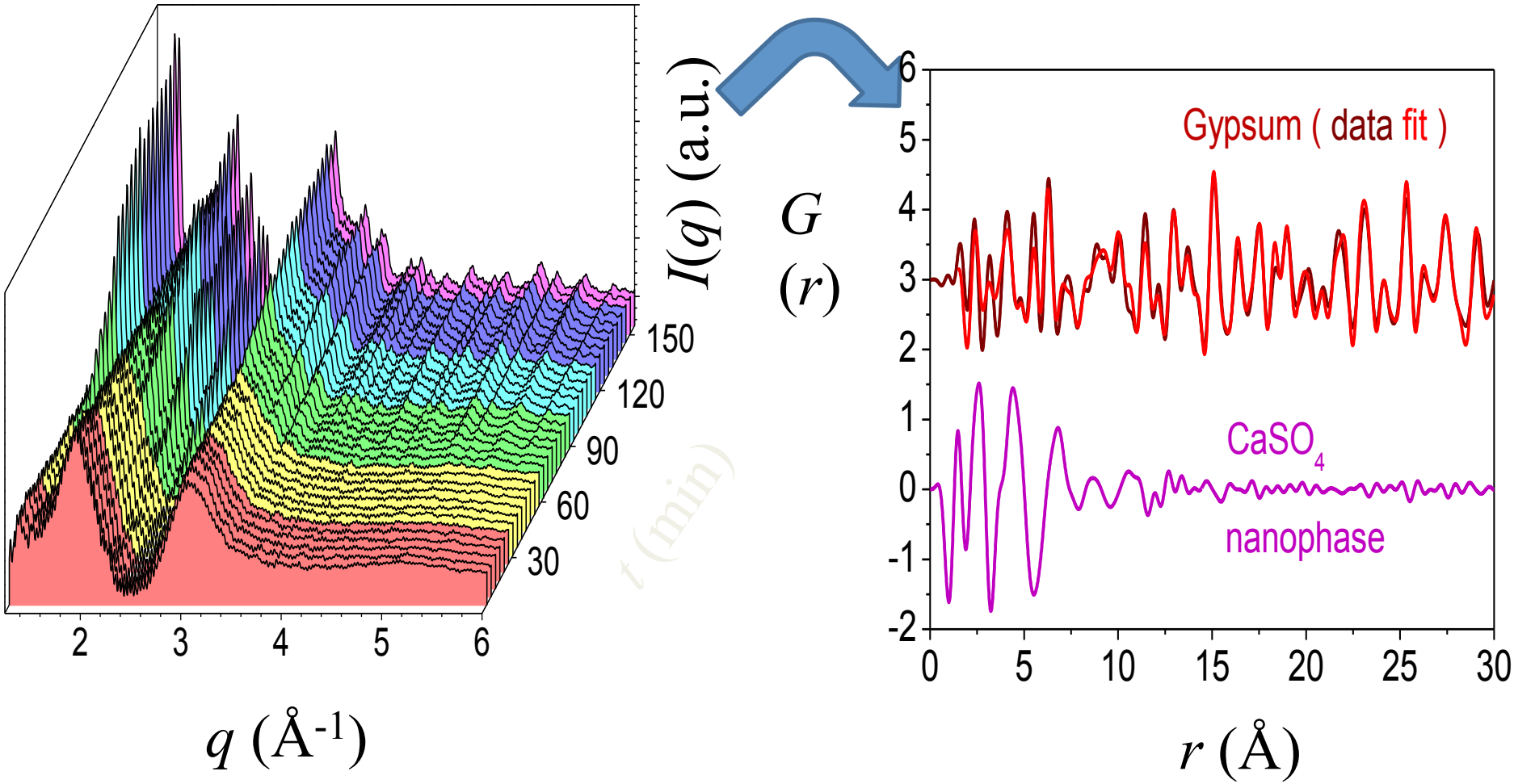
$d \approx$ 0.25 nm

$S(q)$: Structure factor



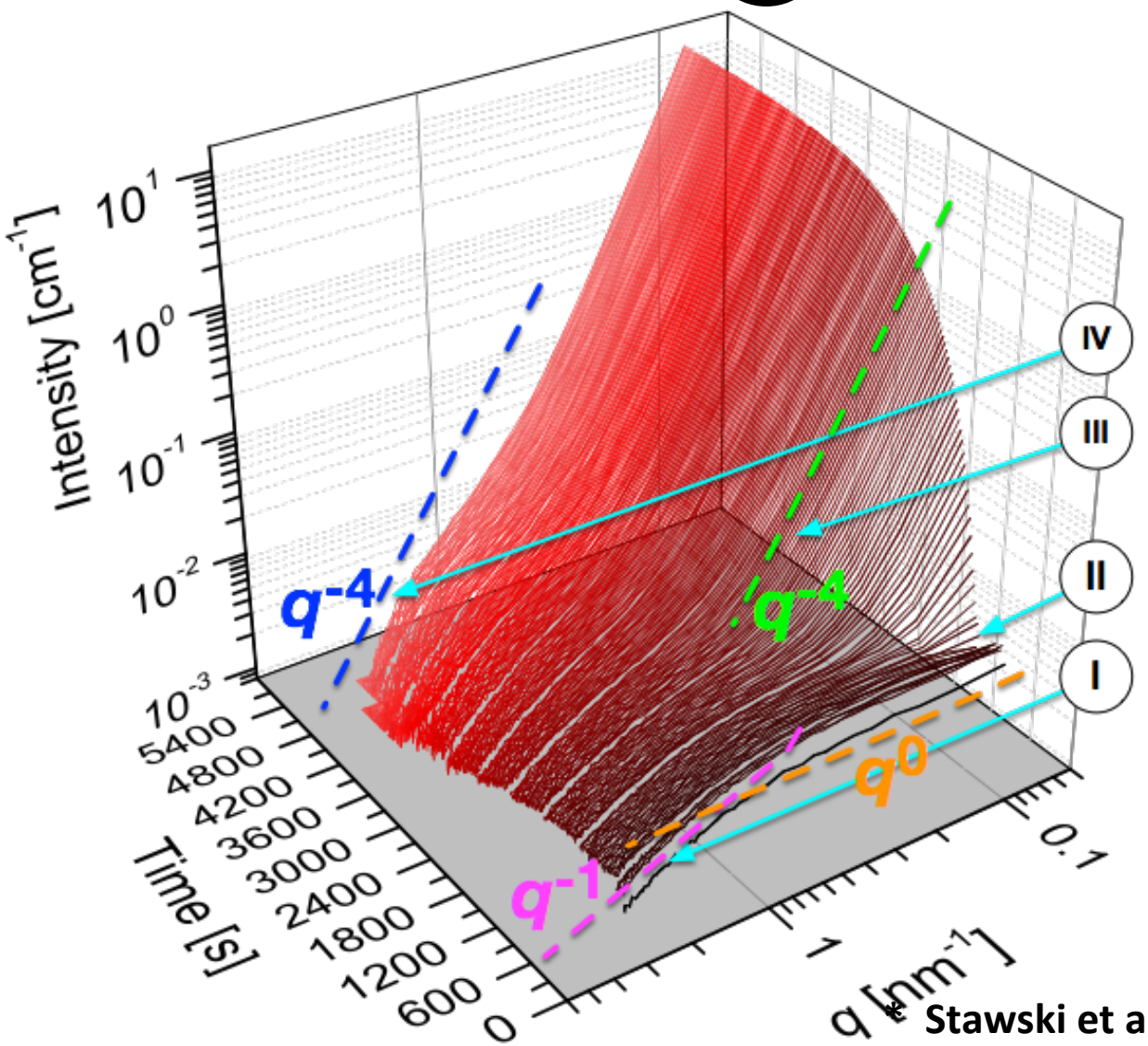
Total scattering → Pair Distribution function
$CaSO_4$ nanophase → Gypsum

Inverse Fourier Transform



Crystallization to Gypsum !

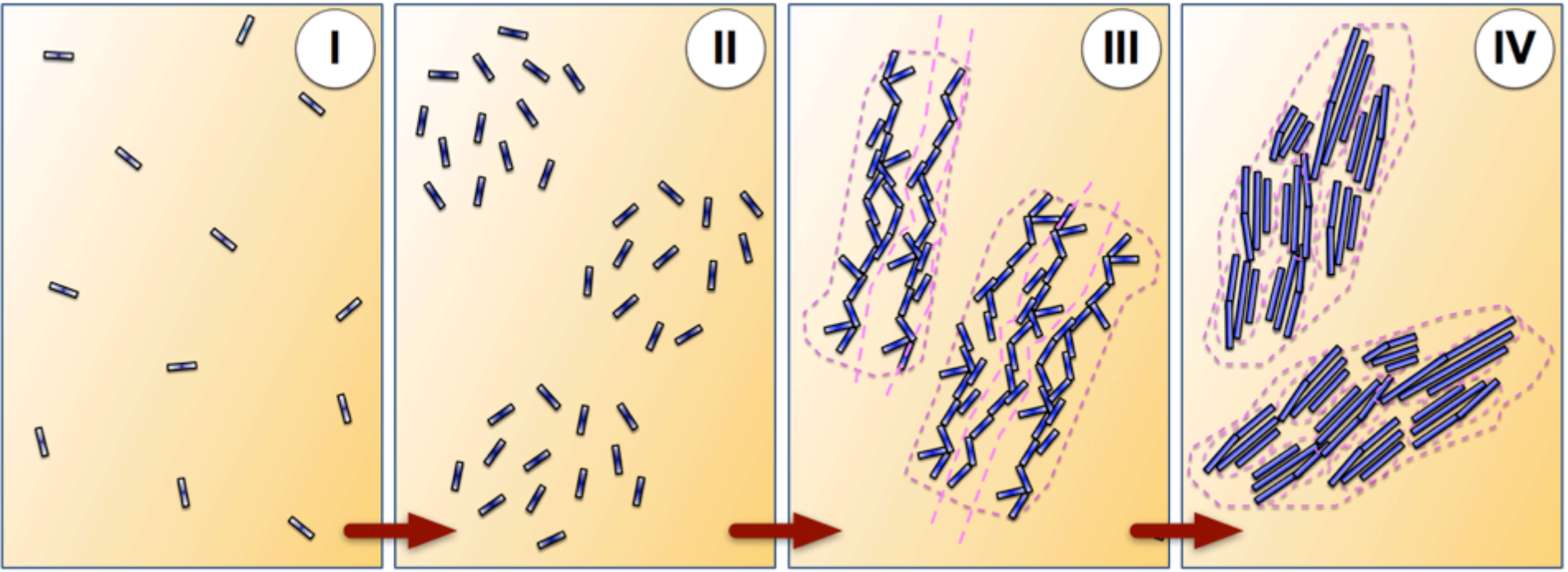
➡ **End of Stage III + Stage IV**



= WAXS: gypsum

* Stawski et al., *Nature Com*. 7 (2016) 1177

Mechanism



SAXS / Total Scattering
pre-gypsum framework

WAXS
Gypsum

* Stawski et al., *Nature Com*. 7 (2016) 1177

Nano-Crystals to Mega-Crystals! Lab *vs.* Nature!

Large gypsum crystals in the Cave of Crystals, Naica, Chihuahua (Mexico)

Assembled bassanite nano-crystals, just before transforming to gypsum

From ions to crystalline gypsum

- Making and re-making bonds
  - 4 distinct stages
- Well defined, elongated $CaSO_4$ nanoparticles
- Growth, aggregation – bricks-in-the-wall assembly
- Crystallization
- NO ACS but nanocrystalline $CaSO_4$ phase

Case Study 2:

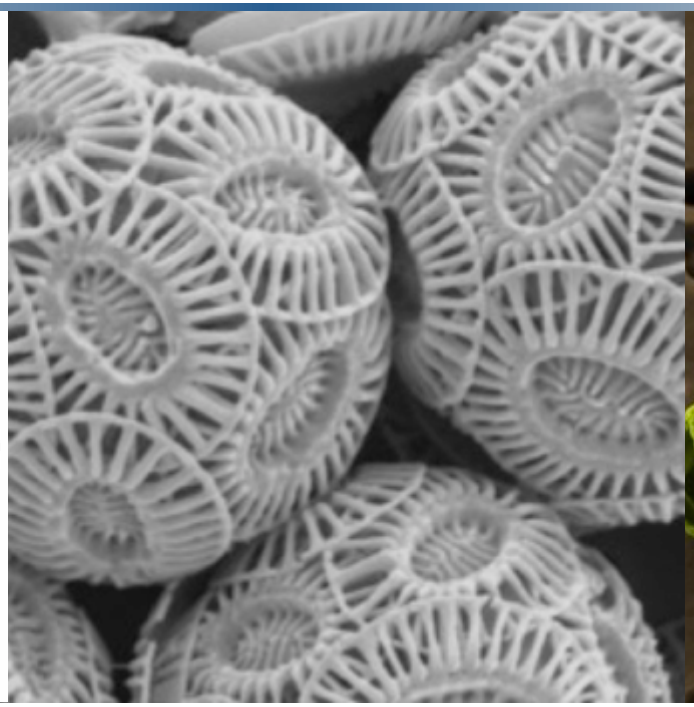
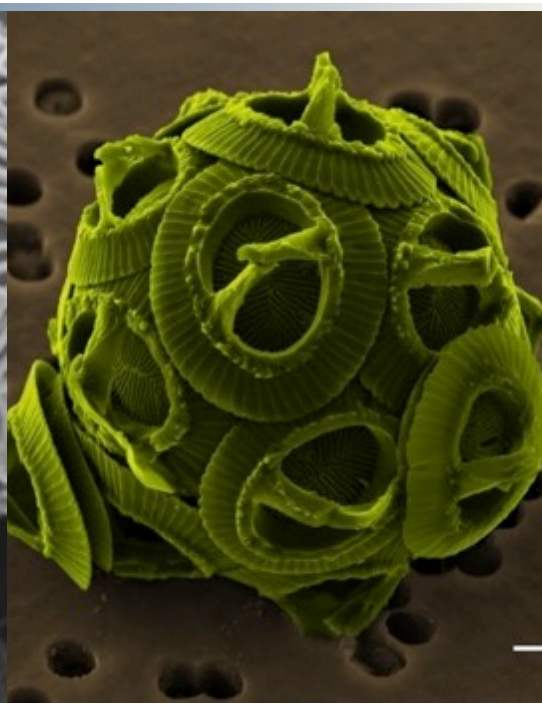
$CaCO_3$ in modern and ancient seas?

Coccolithophore Calcite accumulation rate

= 750 Mio Tonnes / year

~ 6 x 10^{25} liths/year (100* Avogadro's Number/year)

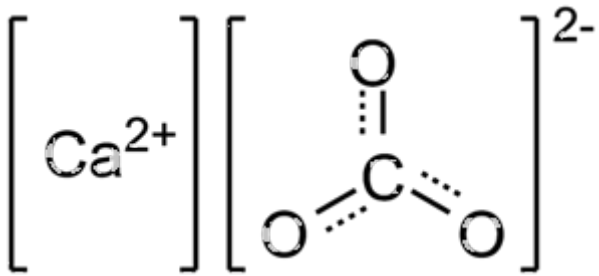
Complicated chemistry of 'simple' things

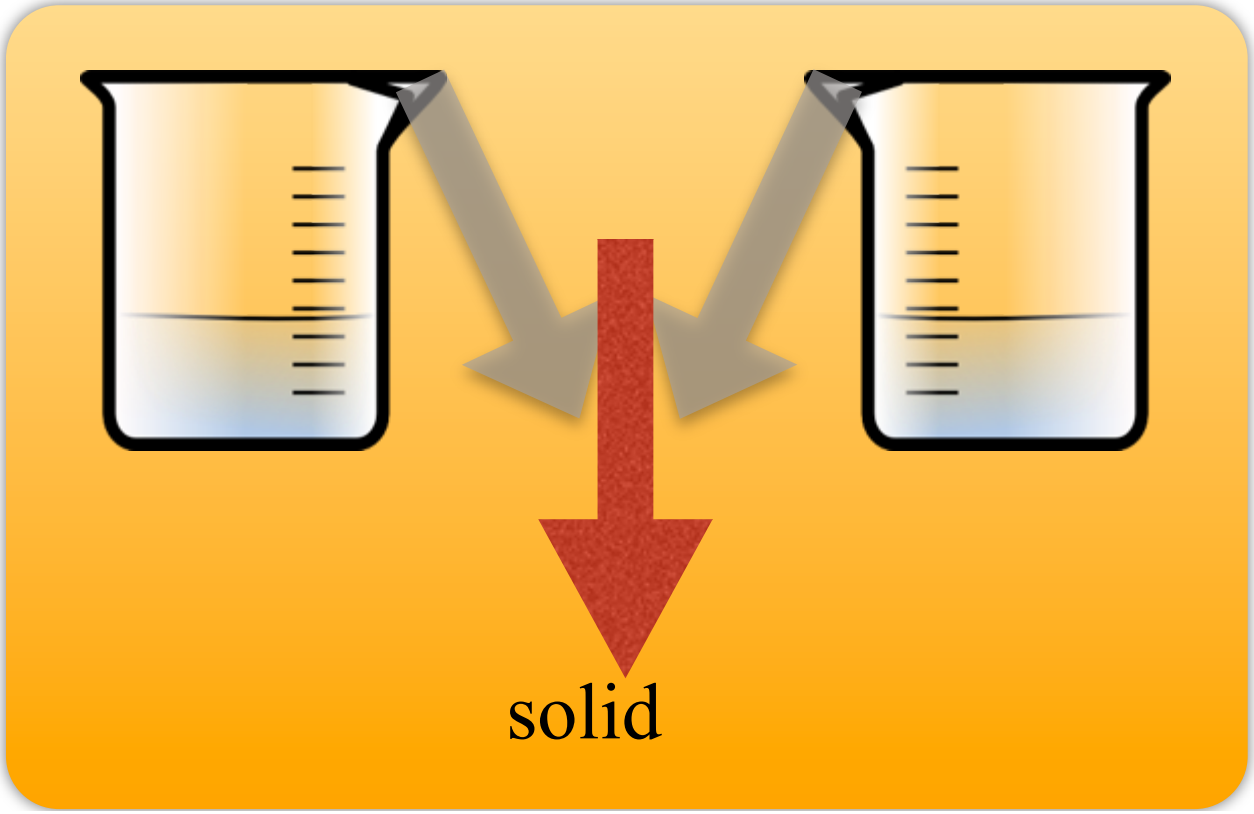



➡ **Understanding** and **controling** nucleation and growth processes is not trivial.

- **How does a coccolith make a lith !**
  - ***Organic / Inorganic interface reaction***
    - ***biomineralization + global C cycle***

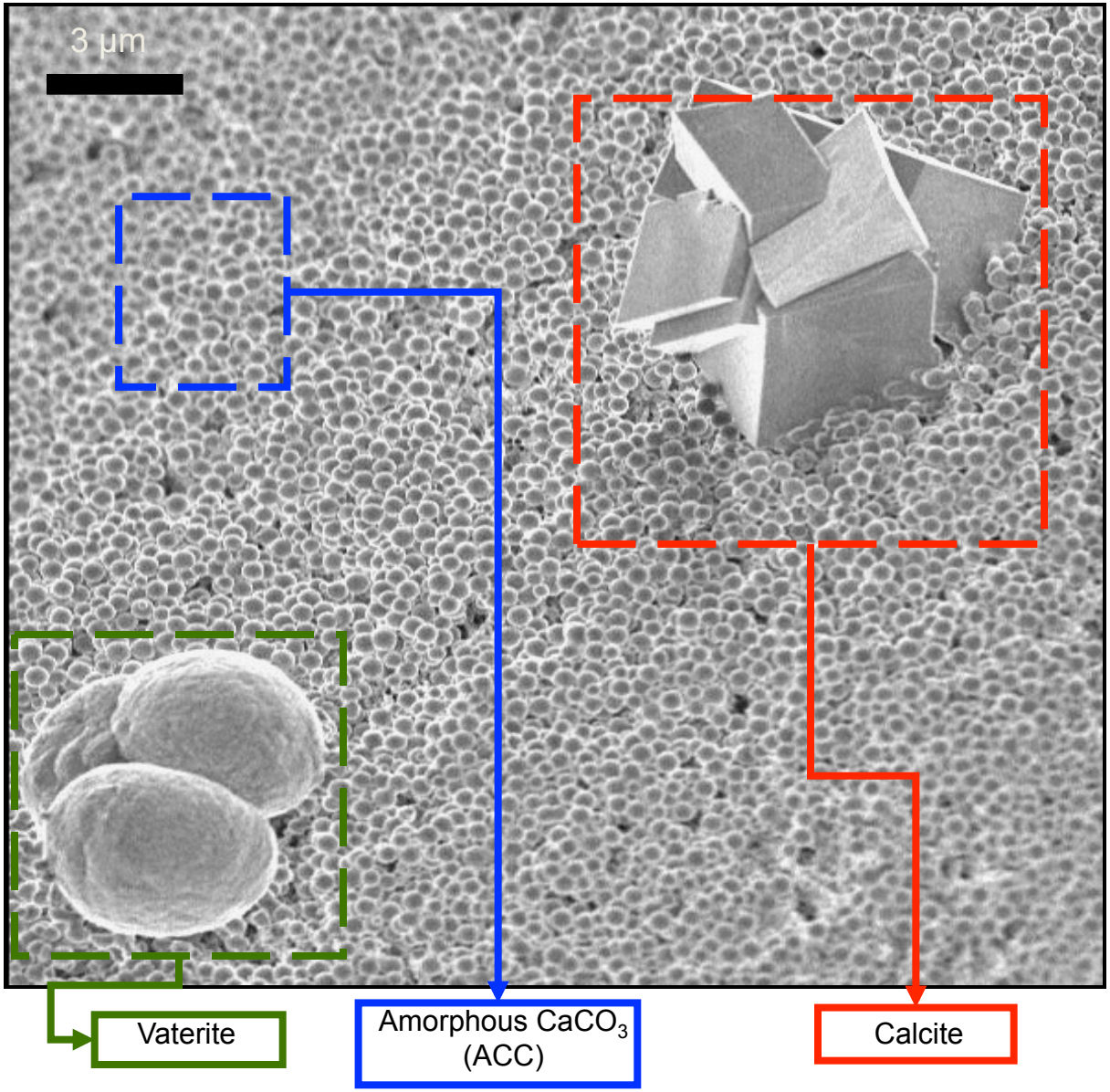
What happens inorganically?





Solution ➟ Clusters ➟ amorphous CC ➟ Vaterite ➟ Calcite

$CaCO_3$ formation - inorganic



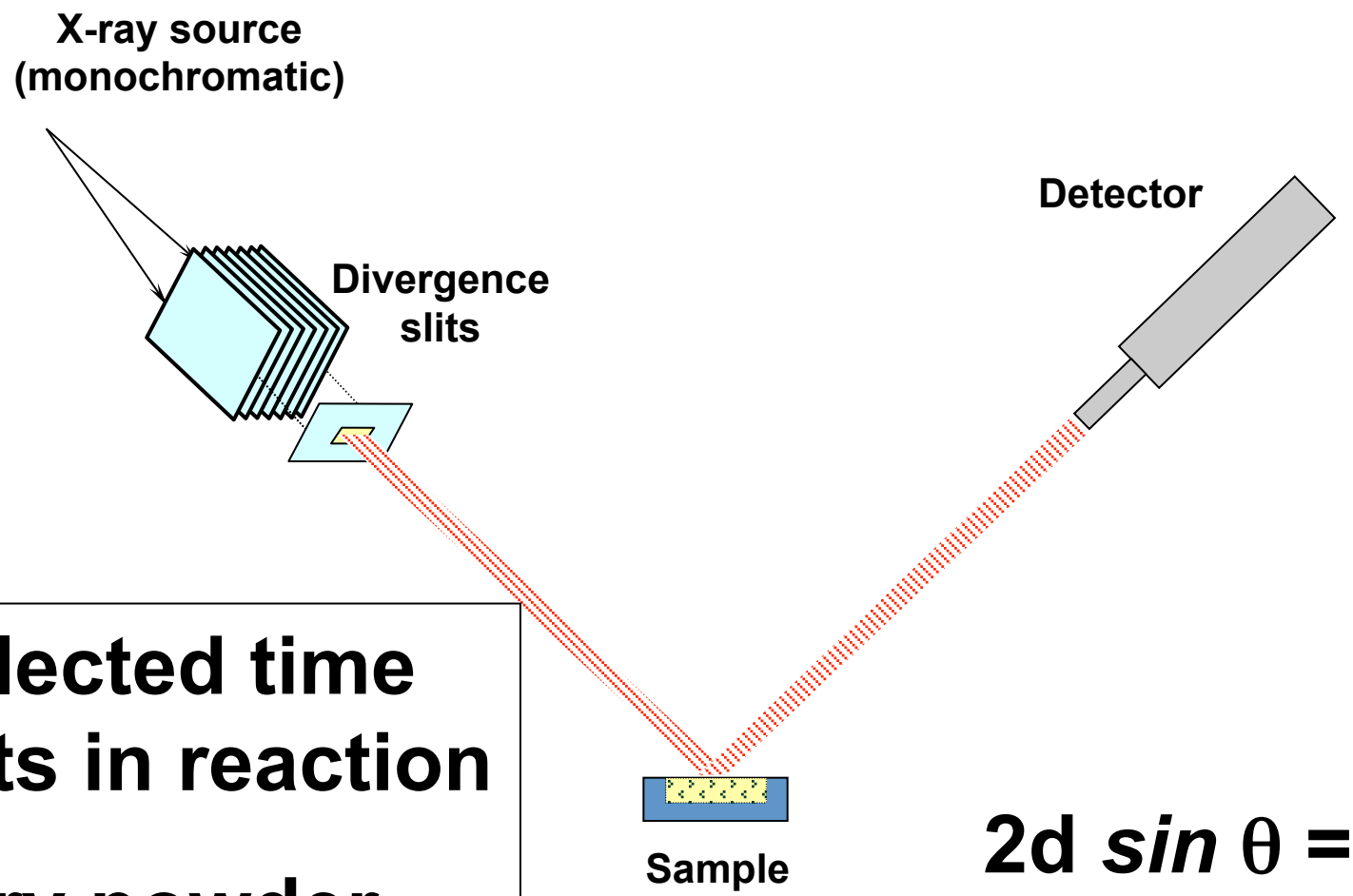
- quantify the mechanisms, kinetics and energetics.

Amorphous -> crystalline

Crystalline -> Crystalline

Conventional PXRD

PXRD



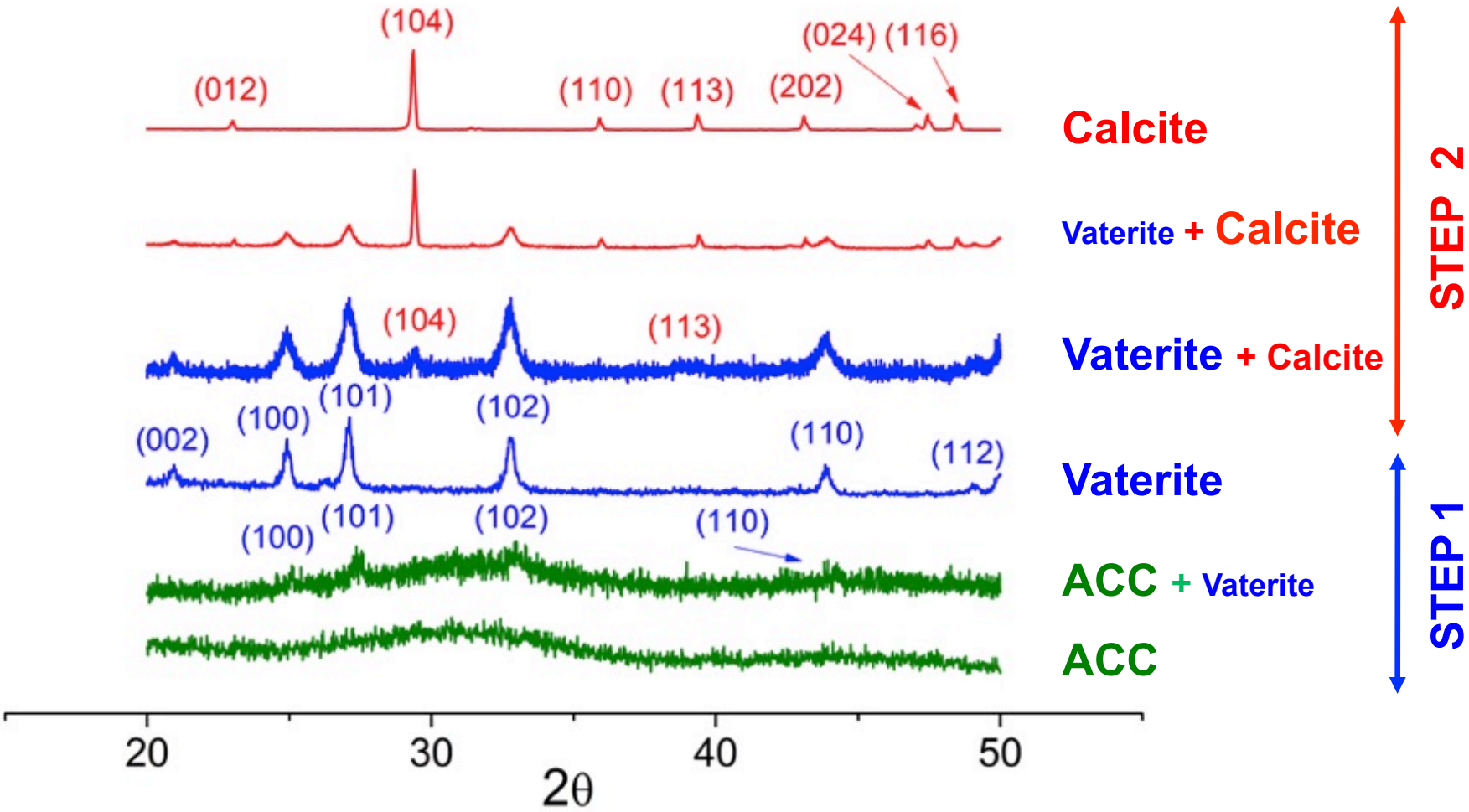
Selected time points in reaction

Dry powder

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

ACC → Vaterite → Calcite

Ex - situ

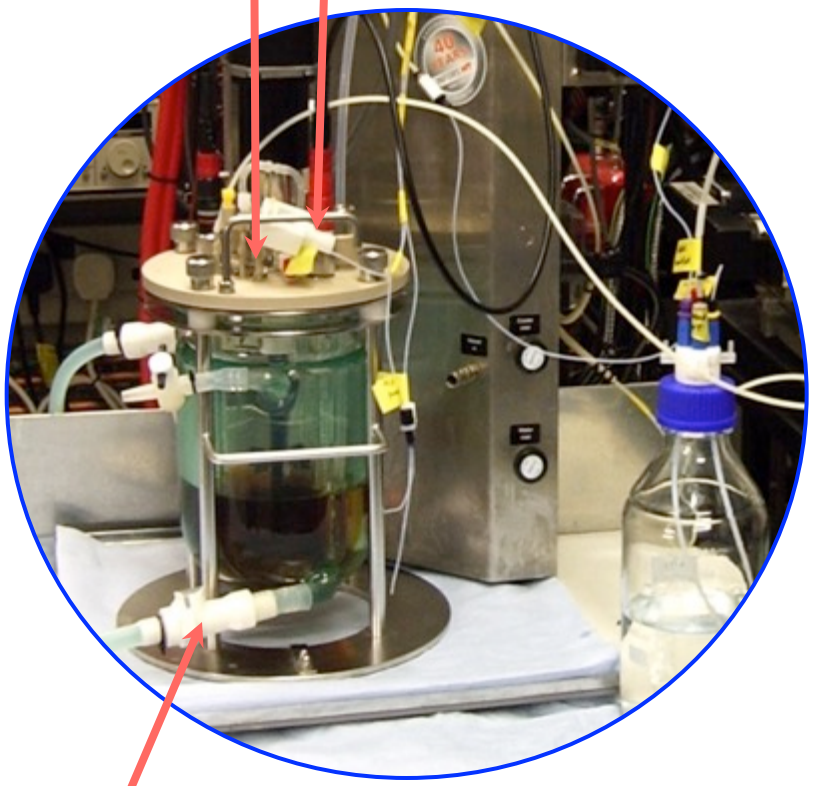


Rodriguez-Blanco et al Nanoscale 2011

Flow through System

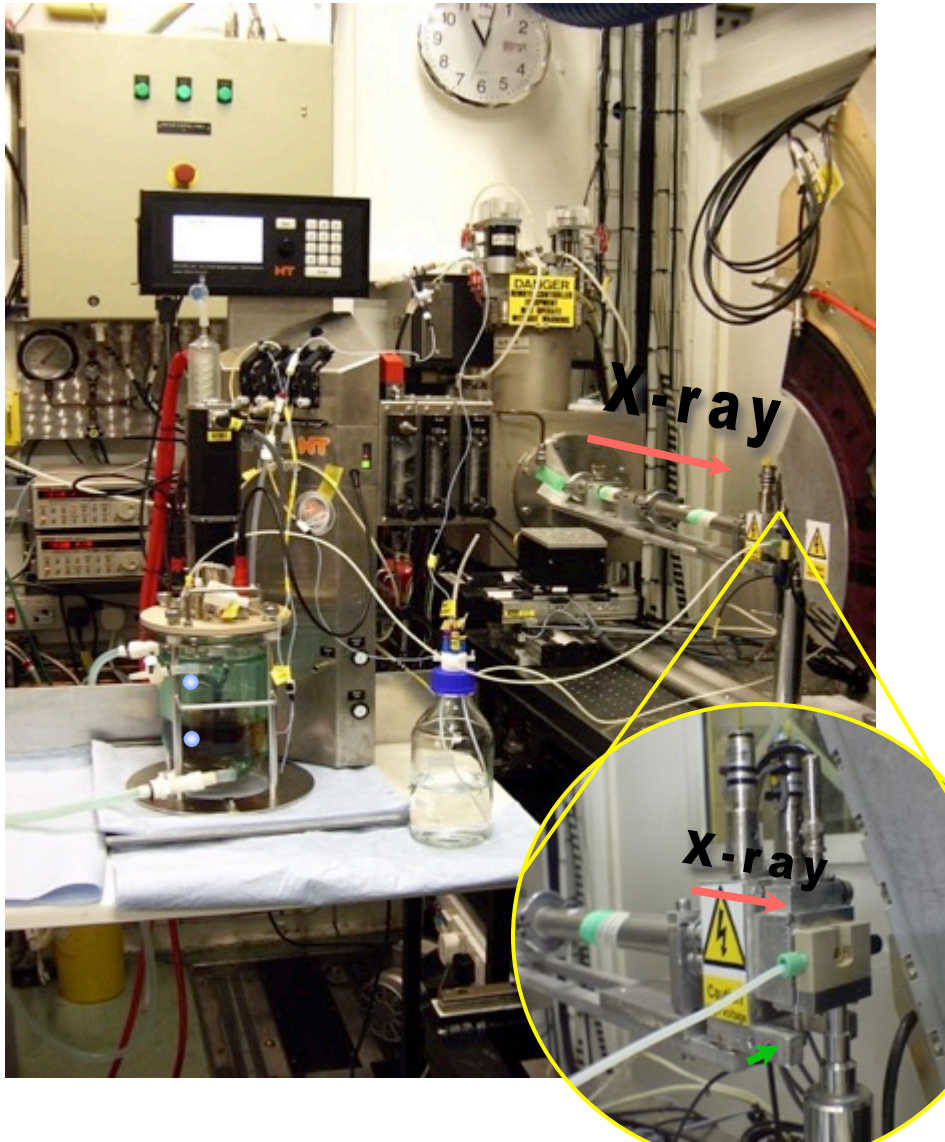
T, redox. pH etc. probes

Oxic/Anoxic (gas-flow)

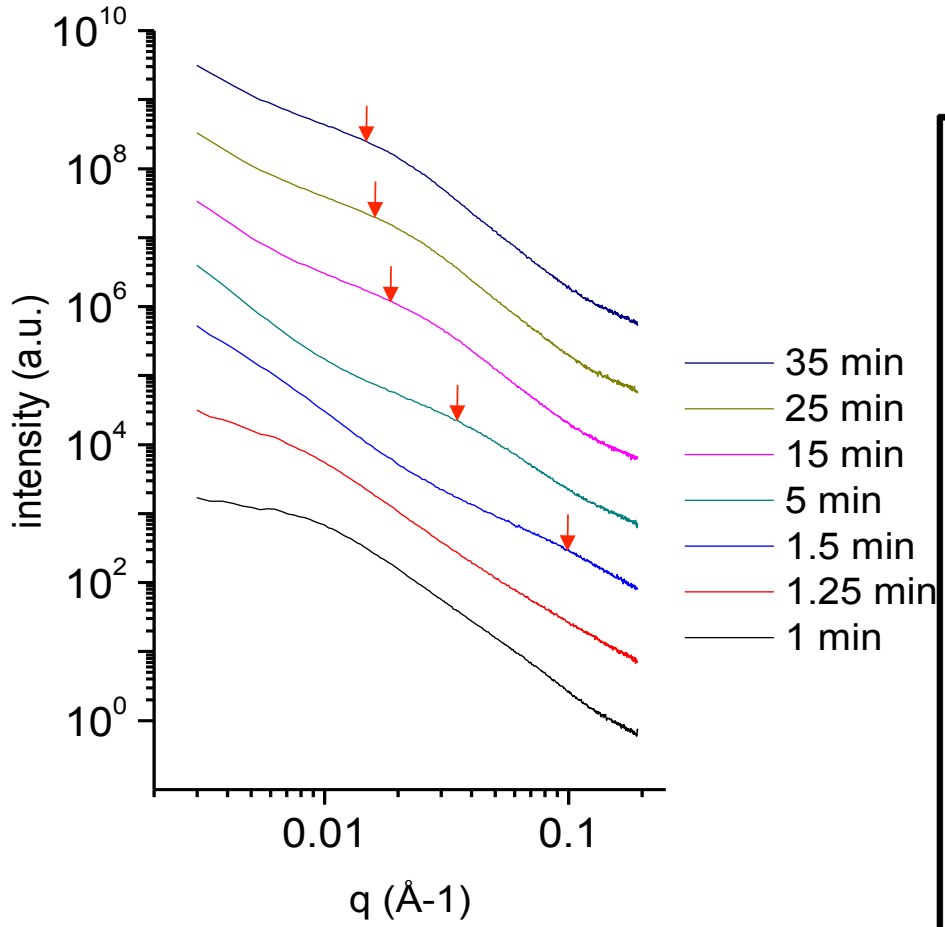


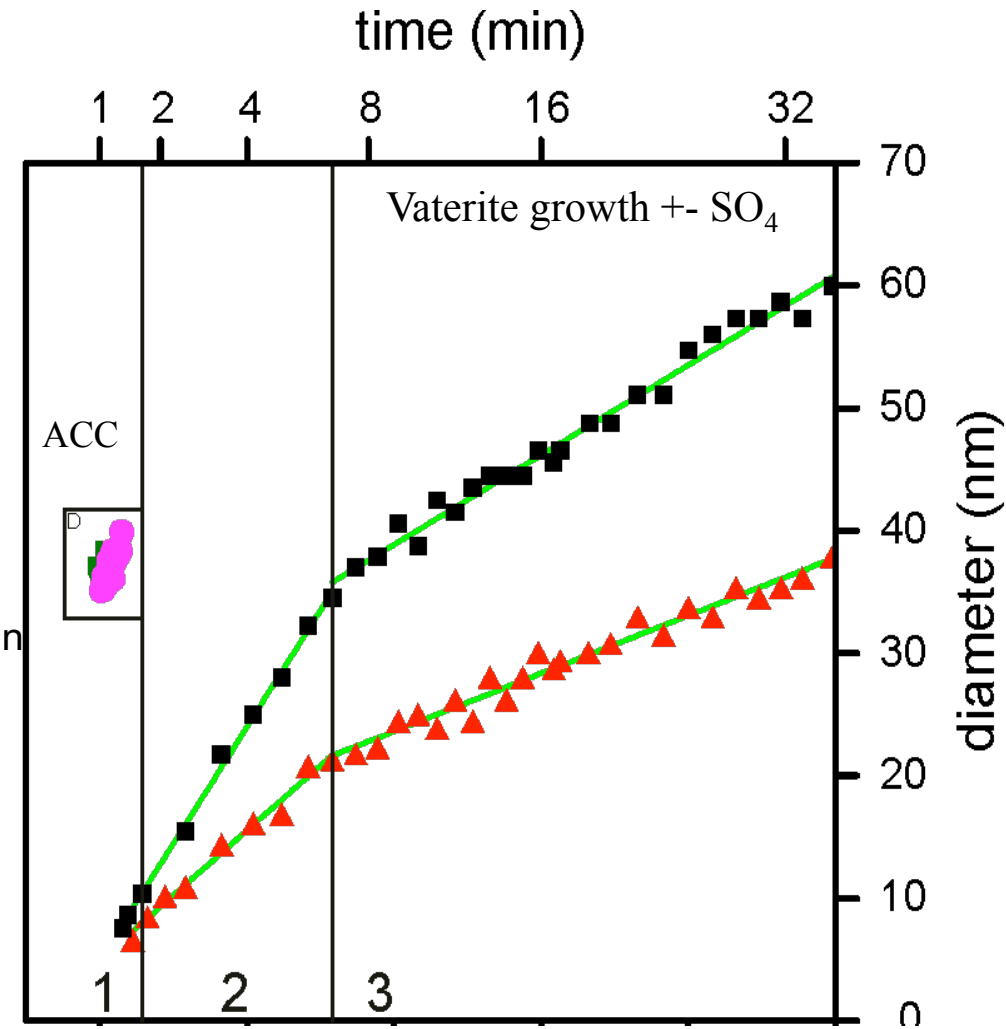
Heating / cooling system

Solution chemistry (pH, Eh, base addition)



Step 1:ACC-> Vaterite (SAXS fast)

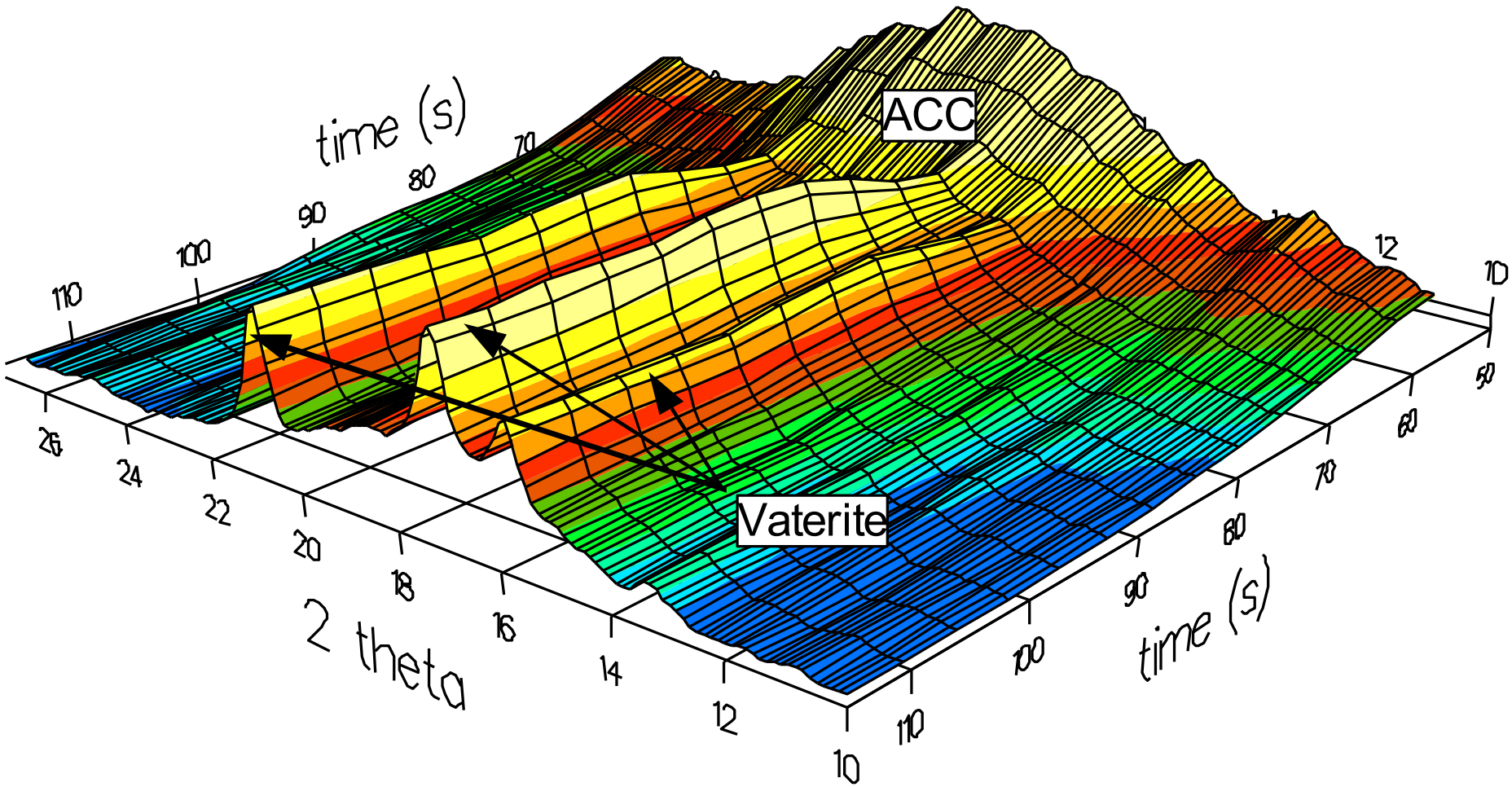




SAXS profile *vs* time

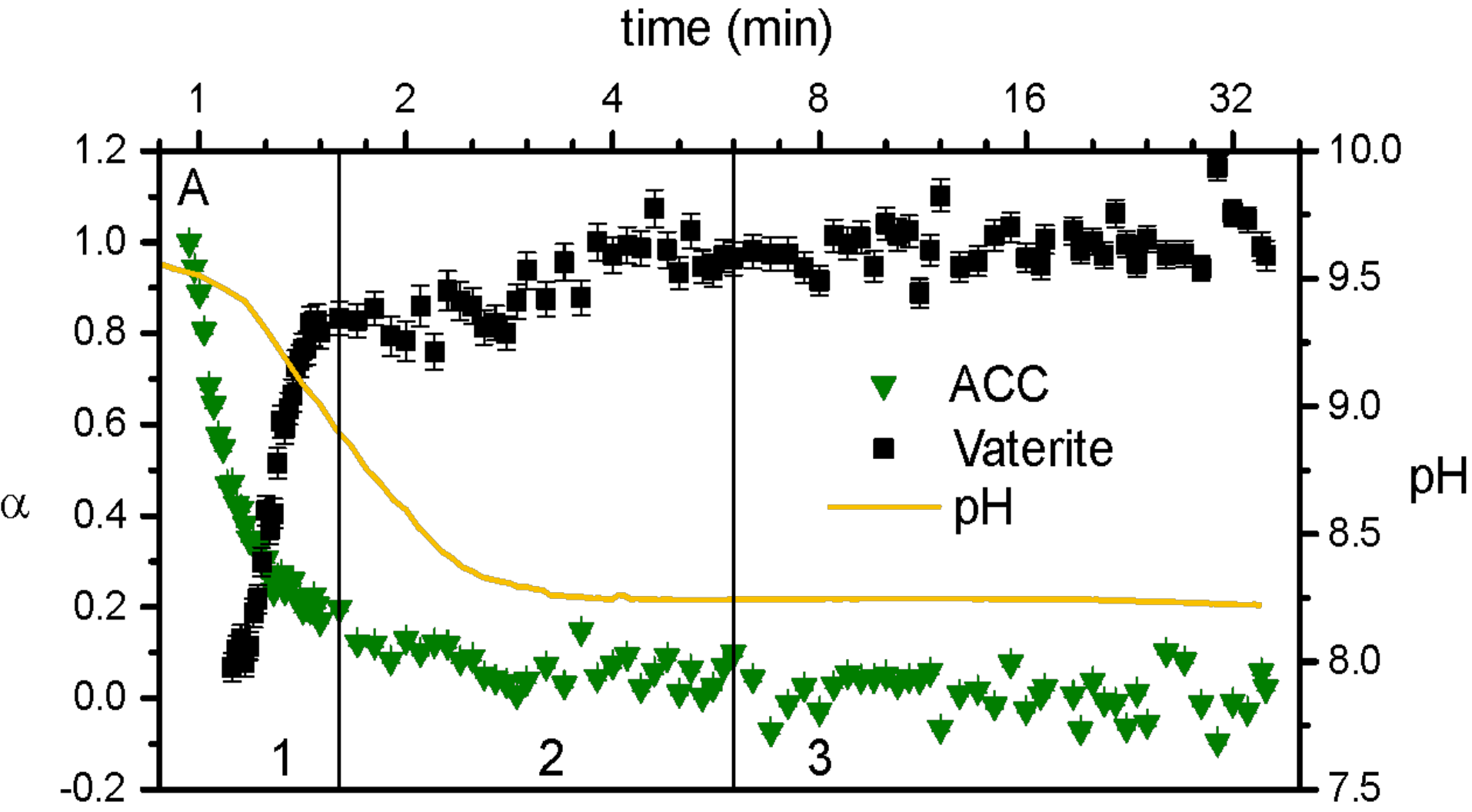
Vaterite crystallite size

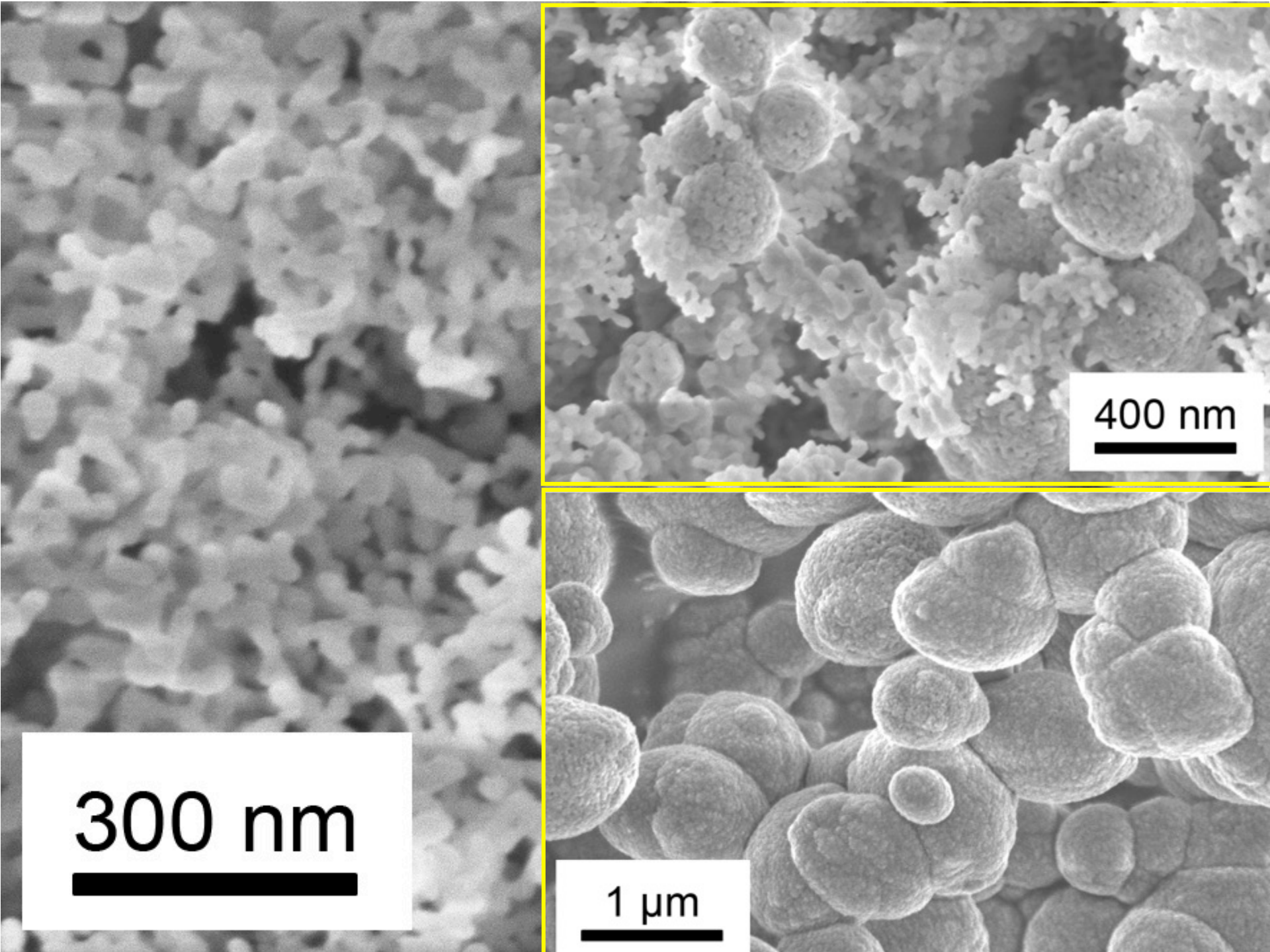
Step 1: ACC➔Vaterite = “Fast reaction”



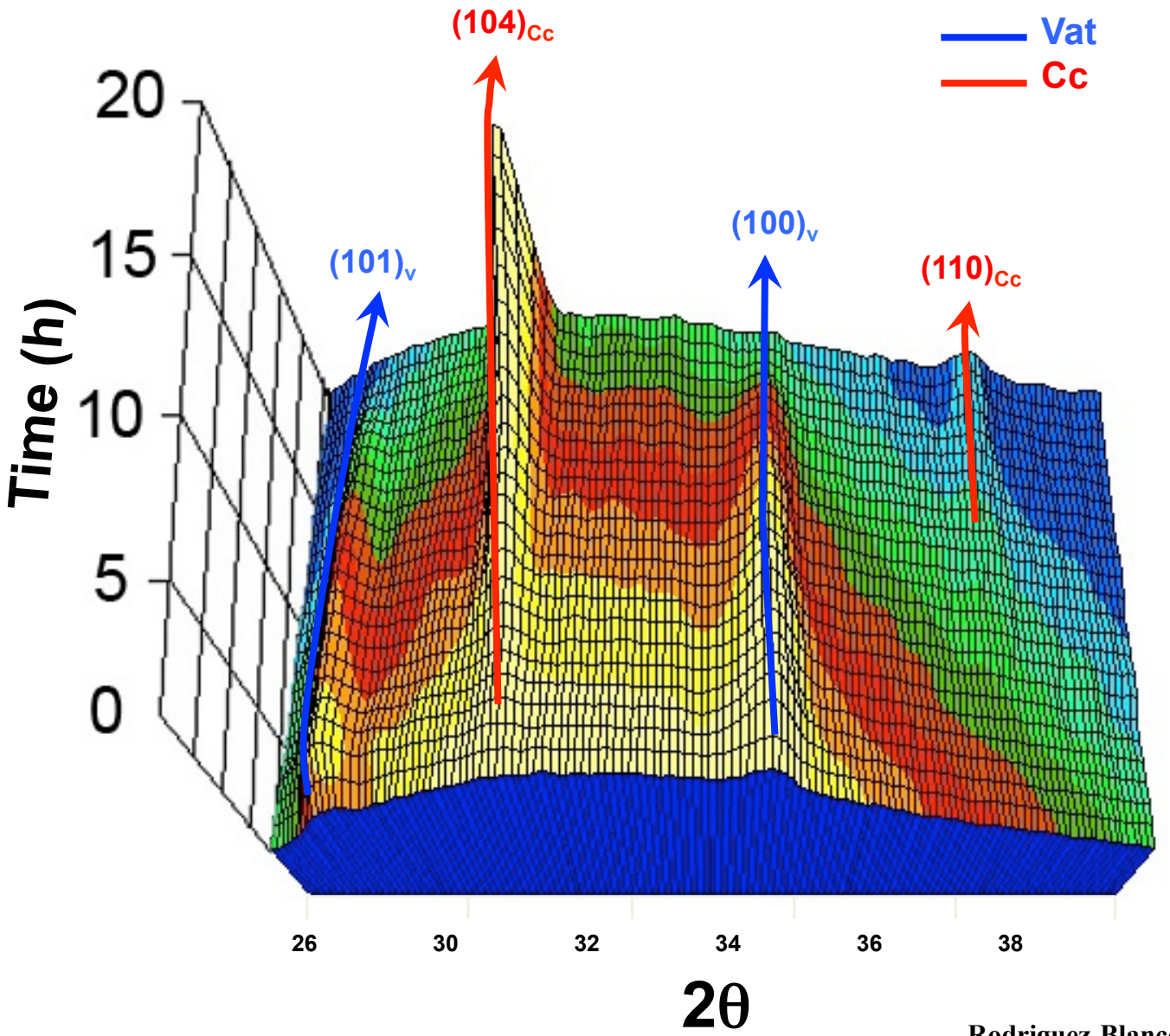
Bots et al CG&D 2012

Step 1: ACC-> Vaterite (WAXS fast)




300 nm
400 nm
1 μm

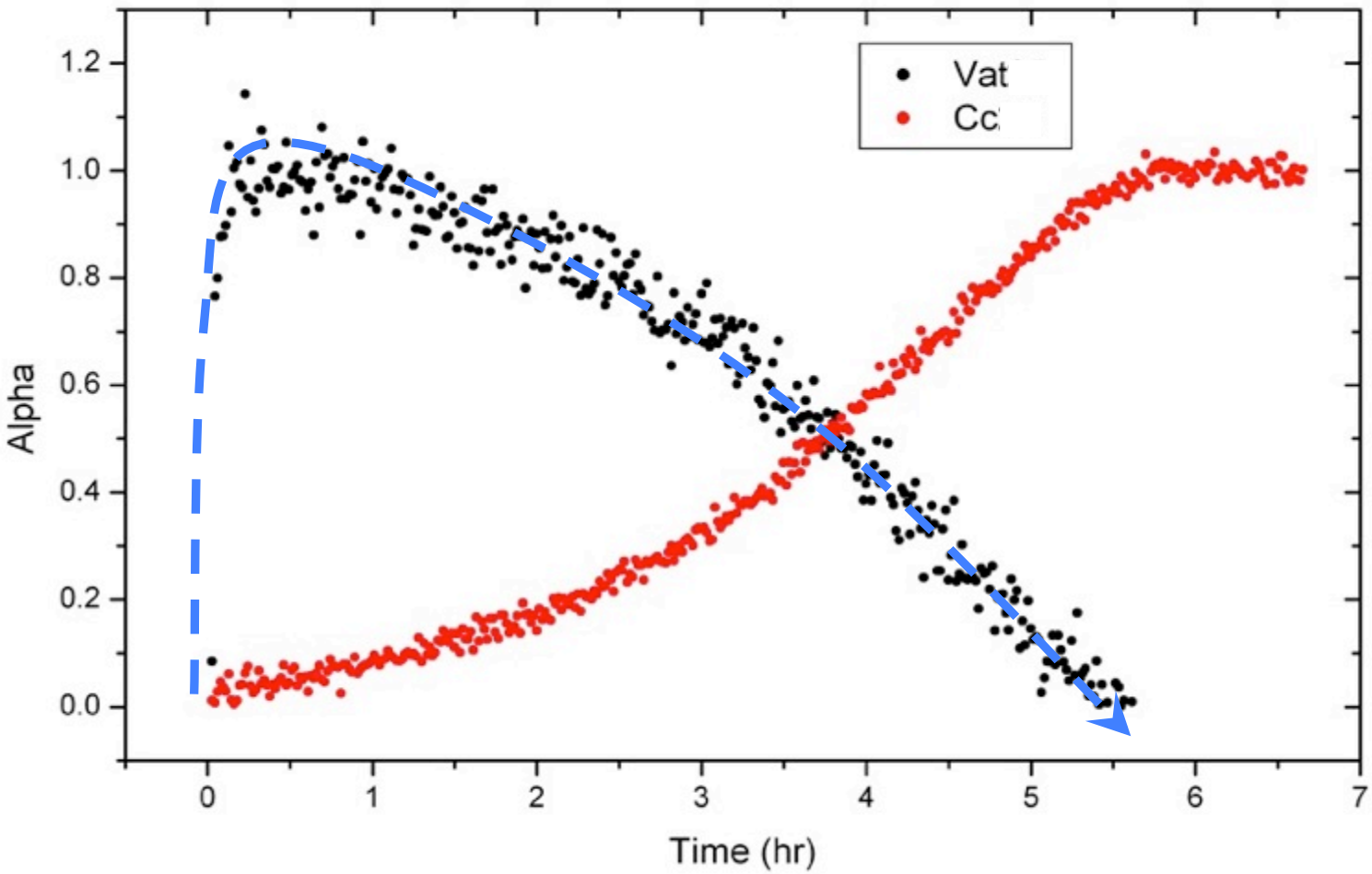
Step 2: Vaterite → Calcite SLOW (er)

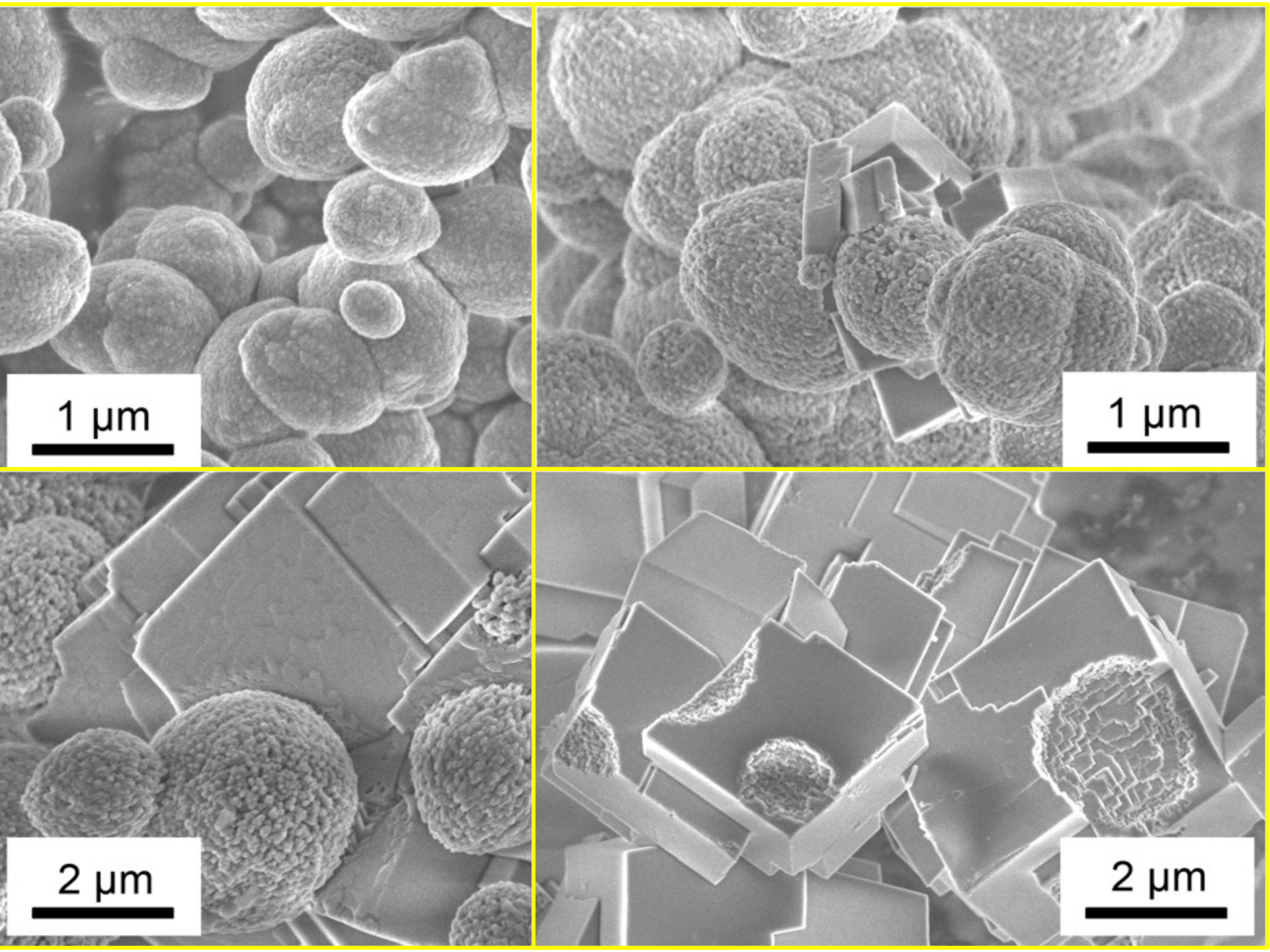


Rodriguez-Blanco et al Nanoscale 2011

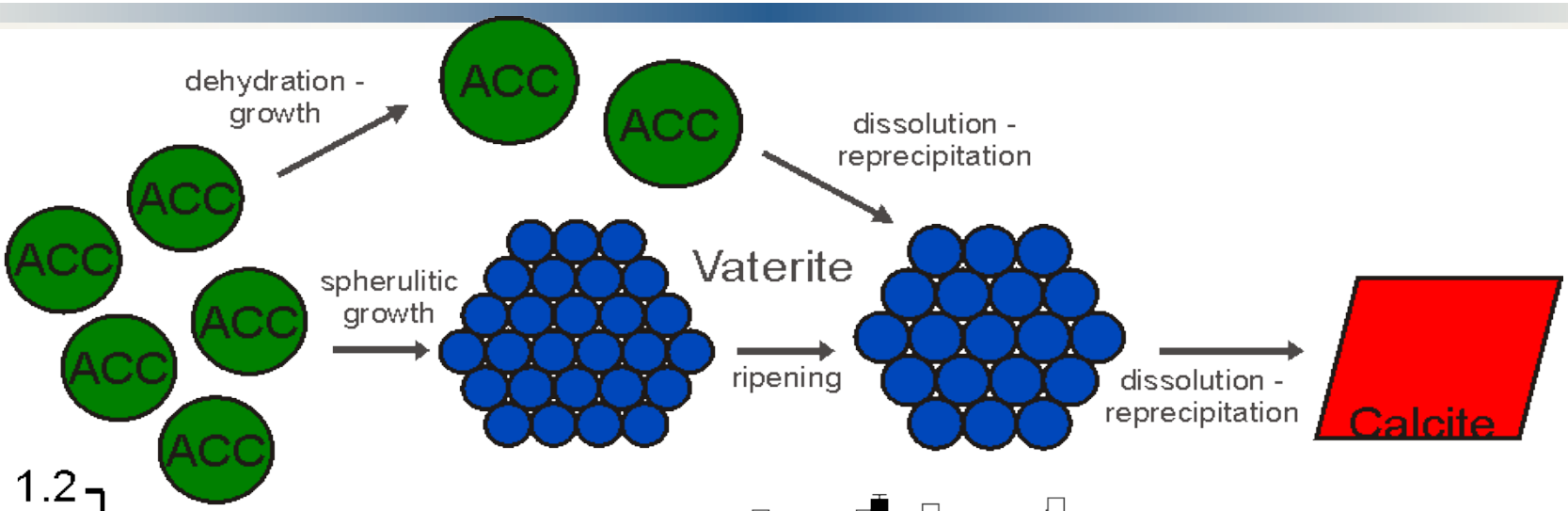
Crystallization path

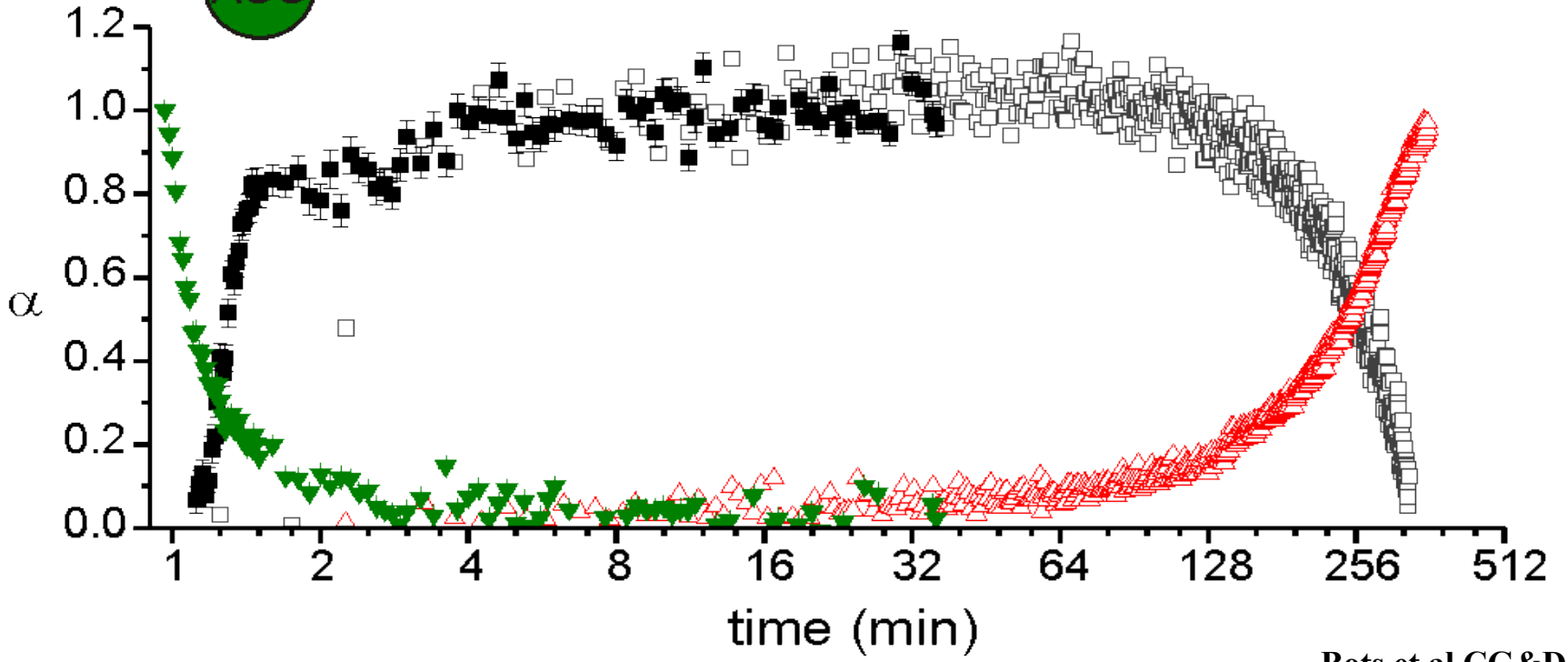
T = 25°C.




1 μm
1 μm
2 μm
2 μm

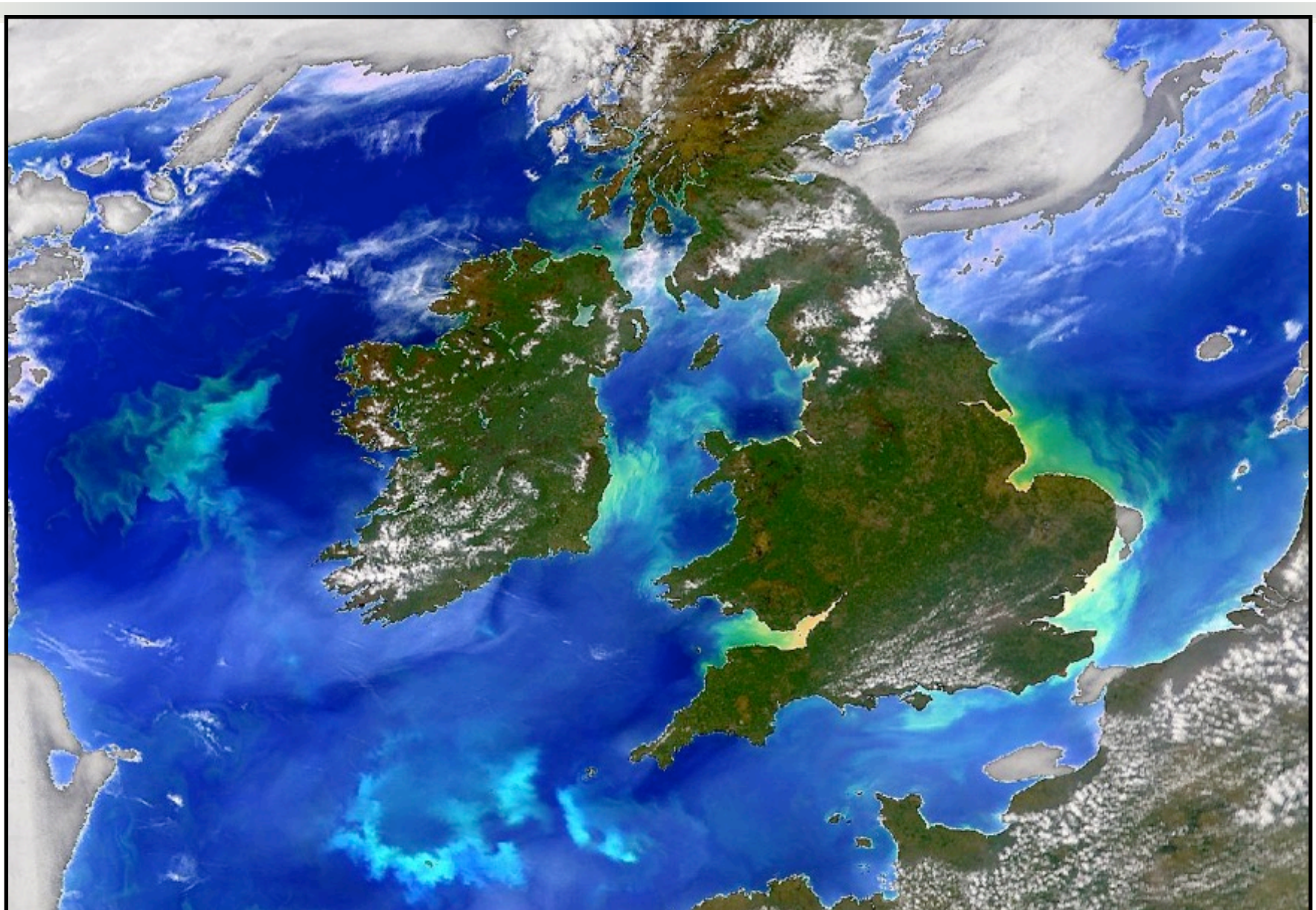
All together now - the inorganic path!



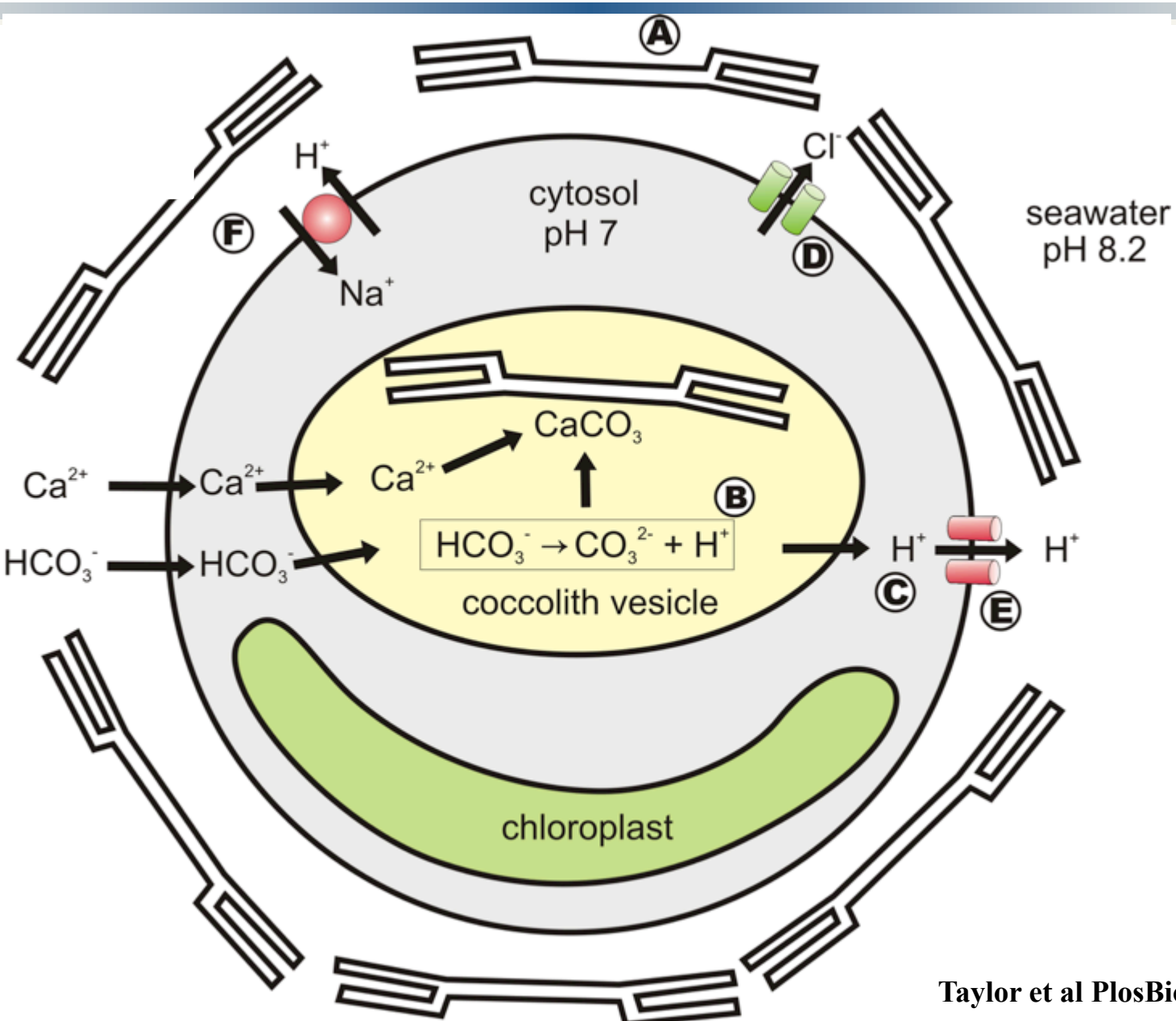


Bots et al CG&D 2012

What happens when life ‘intervenes’?



How does this happen inside a coccolith?



Taylor et al PlosBiol 2011

How does a coccolith do it?

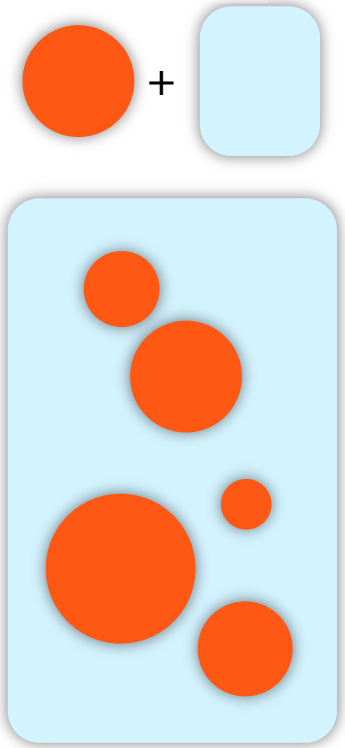
Or …what happens inside an organic “soup”?

8-hour brightfield timelapse.
Cells initially decalcified,
only internal coccolith present.

Alison R. Taylor et al. (2007) European Journal of Phycology 42:125-136

How to we mimic this?
Control nucleation and growth…
…a bit better at least ! Use Micelles !

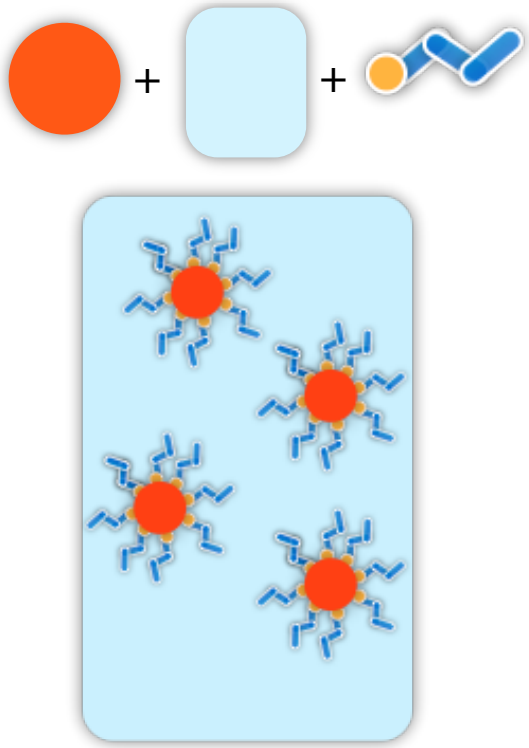
water+ oil



Emulsion

Not spontaneous = Unstable

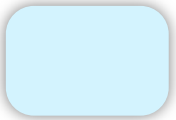
water+ oil+surfactant



Microemulsion

Spontaneous = Stable

If H_2O inside = reverse micelle (RM)



non-polar = "oil"

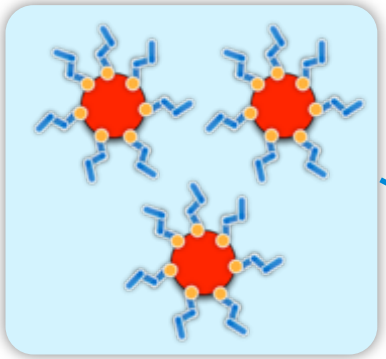
polar = water

non-polar tail

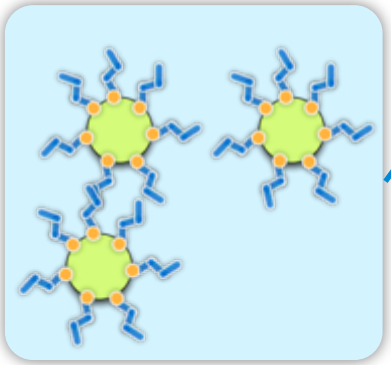
polar head

$CaCO_3$ in reverse micelles?

RM with H_2O +- $[Ca^{2+}]$



RM with H_2O +- $[CO_3^{2-}]$

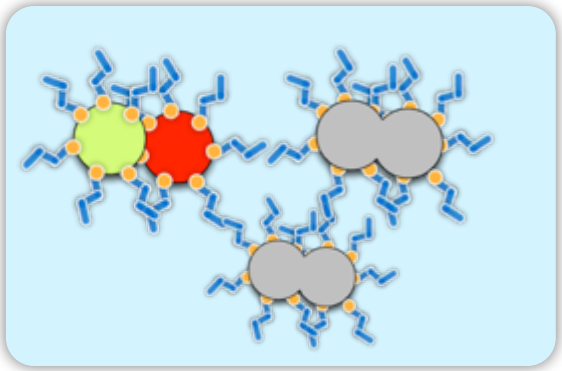


mi ing

PROPOSED MECHANISM

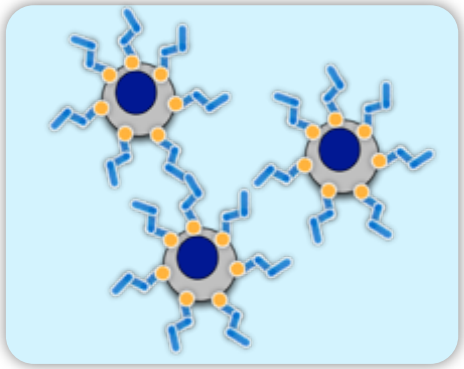
Capek, *Advances in Colloid and Interface Science* 2004

Collision and coalescence of droplets



Diffusion

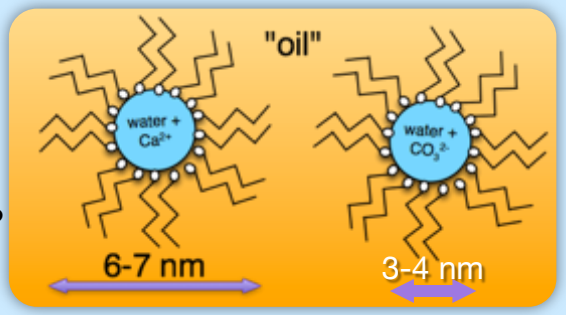
reaction leads to solid particles



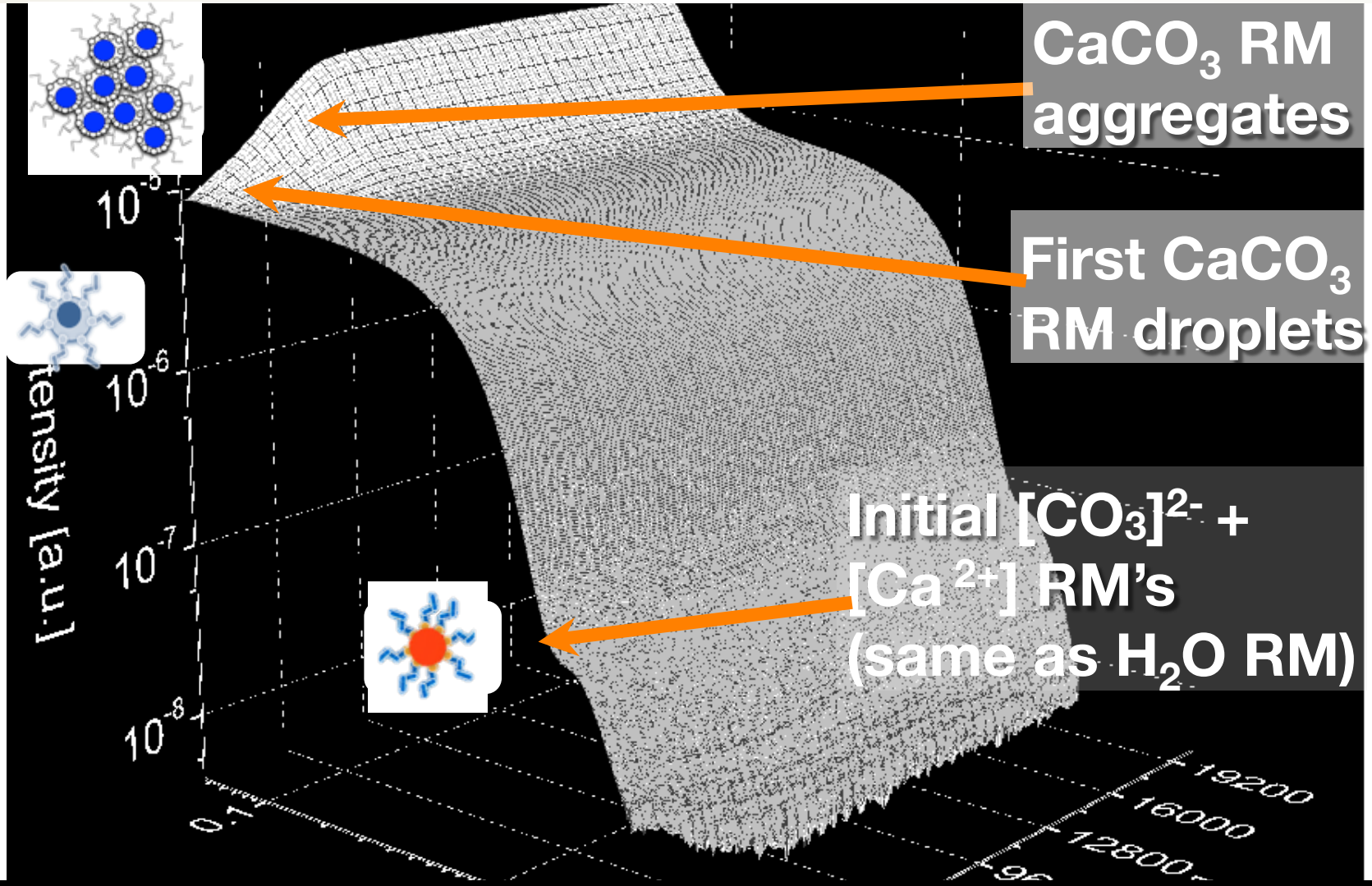
Individual solid particles

notion of a "nanoreactor"

Is mechanisms the same for $CaCO_3$?
$[CO_3]^{2-}$ and $[Ca^{2+}] \leq 0.2M$

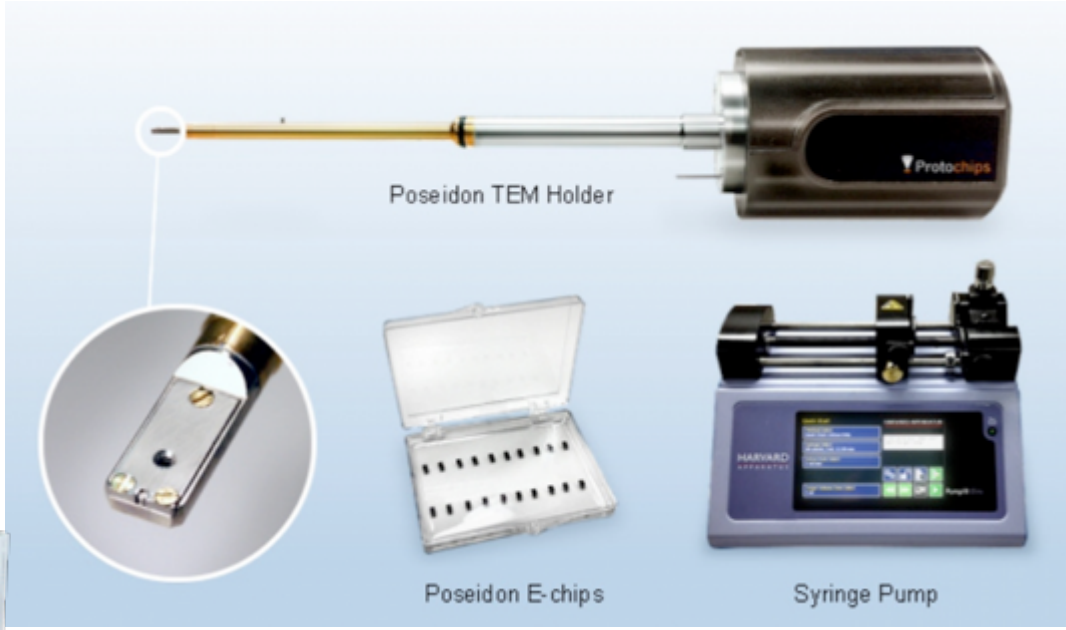


In situ reaction inside micellar nanoreactors - SAXS



$CaCO_3$ RM's are very stable – BUT is structure a liquid-like or solid $CaCO_3$ phase?

How to see what happens in real time? Liquid Cell TEM.

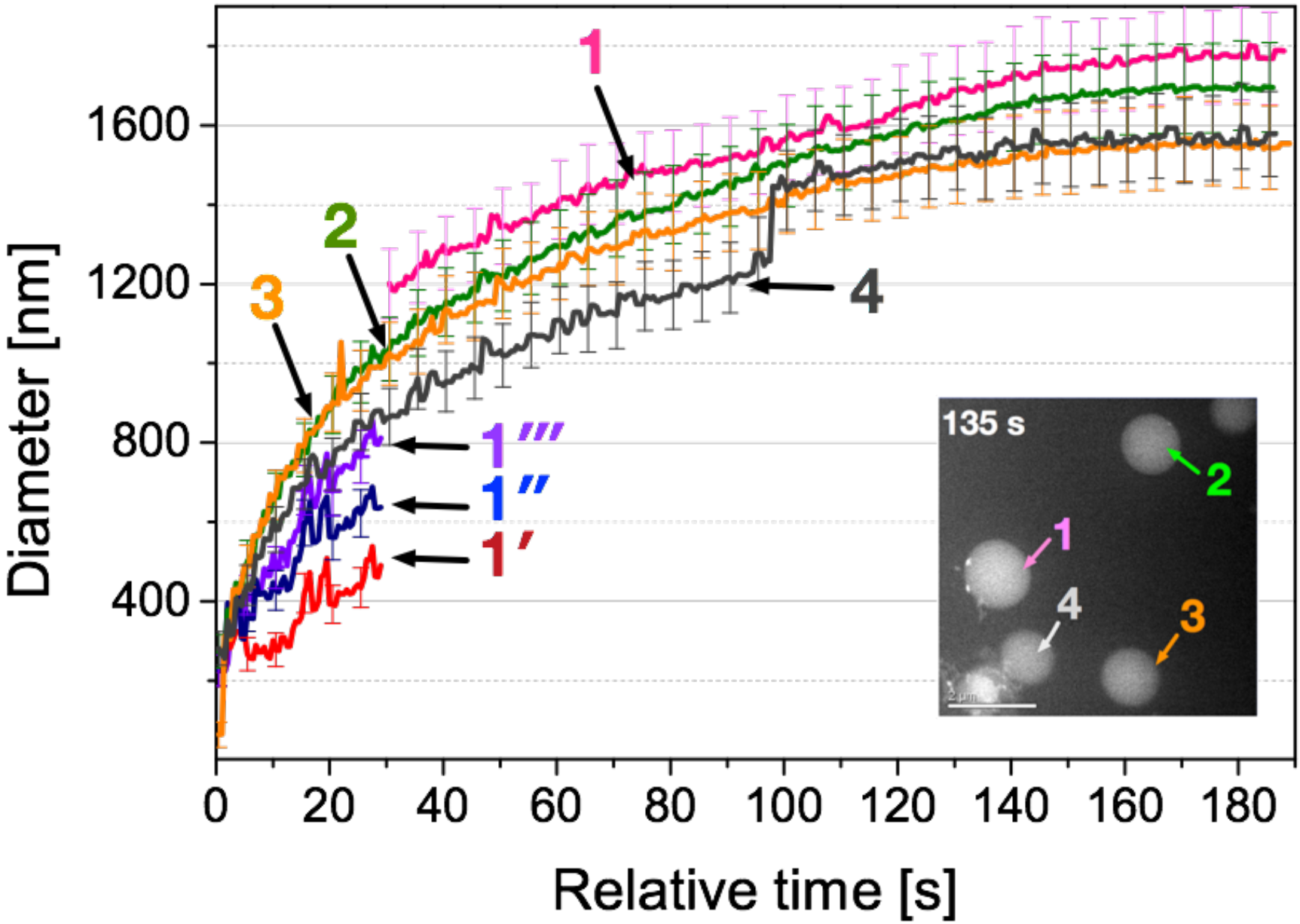


Synthetic organic “nanoreactor”

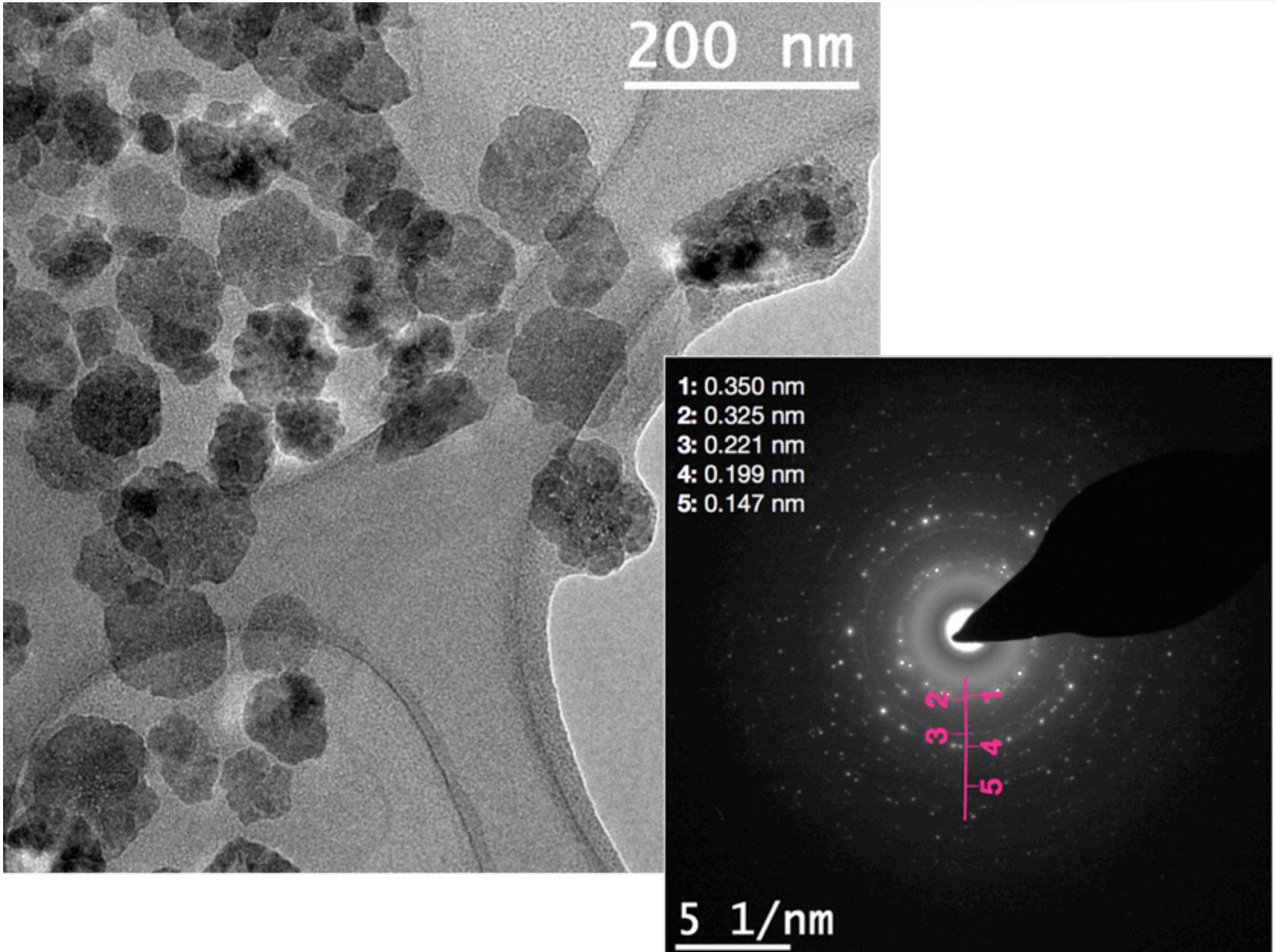
In situ **liquid cell TEM - $CaCO_3$ inside micelles!**

Stawski et al in review

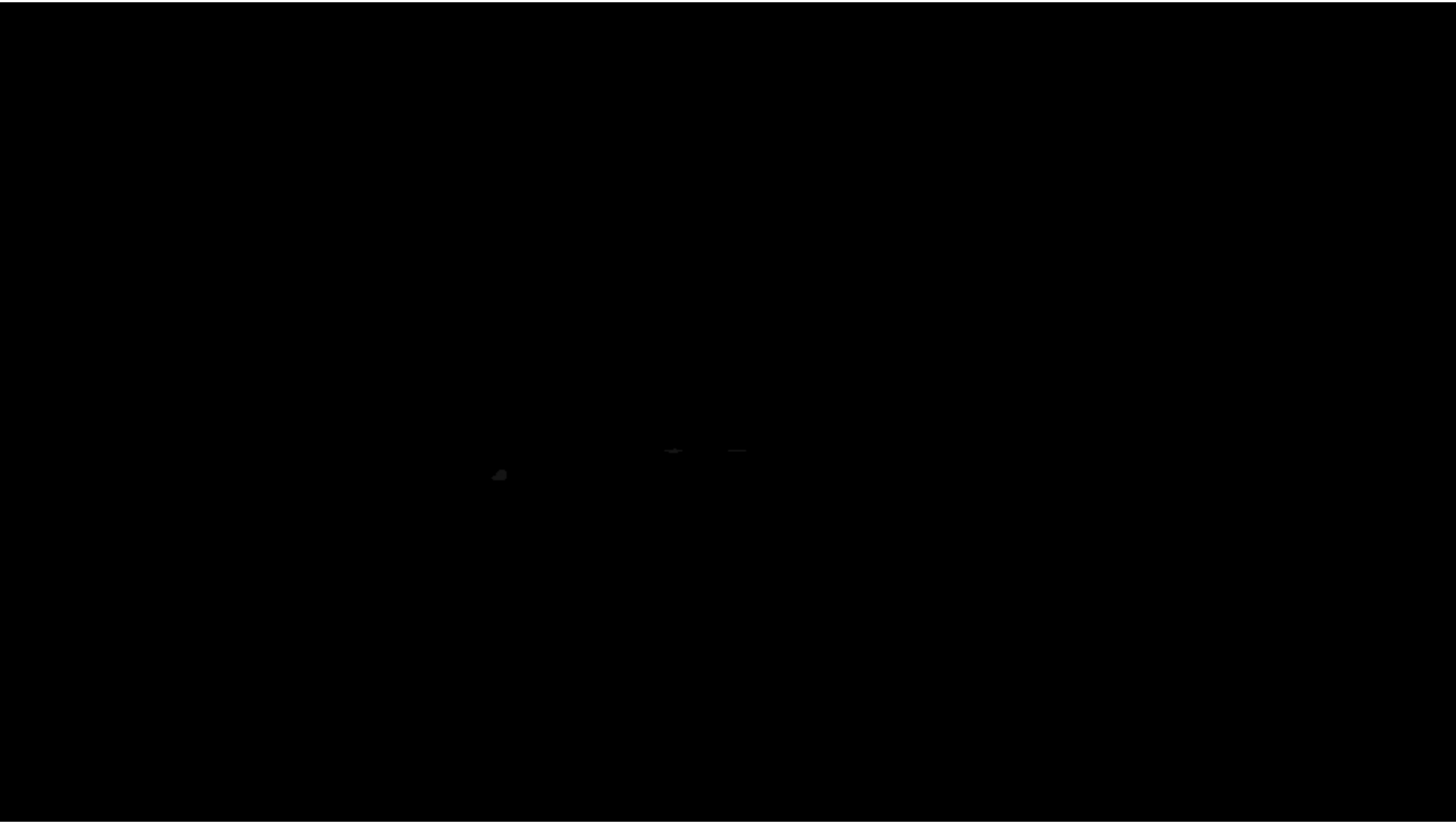
Growth of globules



What is inside the micelles? Ex-Situ



Crystallize "nanoreactor" contents *in situ*



In situ **liquid to solid $CaCO_3$ transformation!**

Summary $CaCO_3$

- Inorganic – process fast:
  - Ions – clusters – ACC – Vat - Cc
- Micelles – nanoreactors = stabilize liq phase:
  - ions – liq phase – (ACC?) Vat - Cc
- Nucleation of a solid phase can be controlled
- Similar to what happens inside coccoliths ?

Summary and the future !

- **Quantifying pathways and mechanisms of mineral formation from ions are key in many natural systems with huge impact on Earth's element cycles in the past, present and future**

- **This knowledge is also crucial for our ability to make novel materials, clean up our environment, to sequester CO_2, or to protect our cultural heritage;**

- **We now have the 'toys' but still need more realistic experimental and theoretical knowledge about fundamental processes… the future is indeed bright!**

Only limitation is our imagination…. and naturally time/money…

Acknowledgements

Benning group : P, Bots, J. D. Rodriguez Blanco, T. Roncal Herrero, M. Ossorio, A. Tomasz Stawski,

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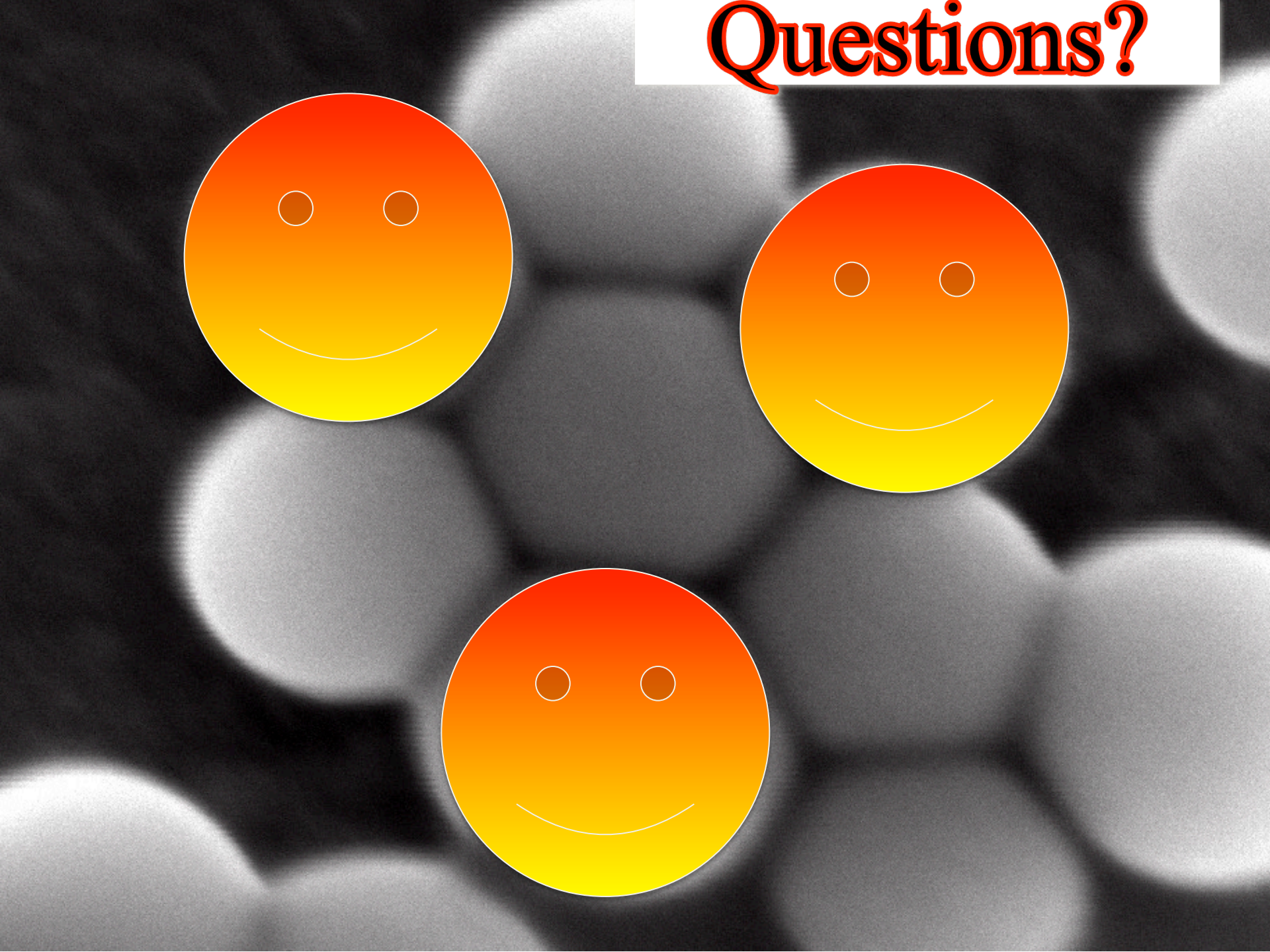
SR-Laboratories: N. Terrill (DIAMOND); A. Fernandez-Martinez (ESRF);

Funding: NERC, UL, EPSCR, CCLRC/STFC; EU; Helmholtz Recruiting Initiative

Questions?



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