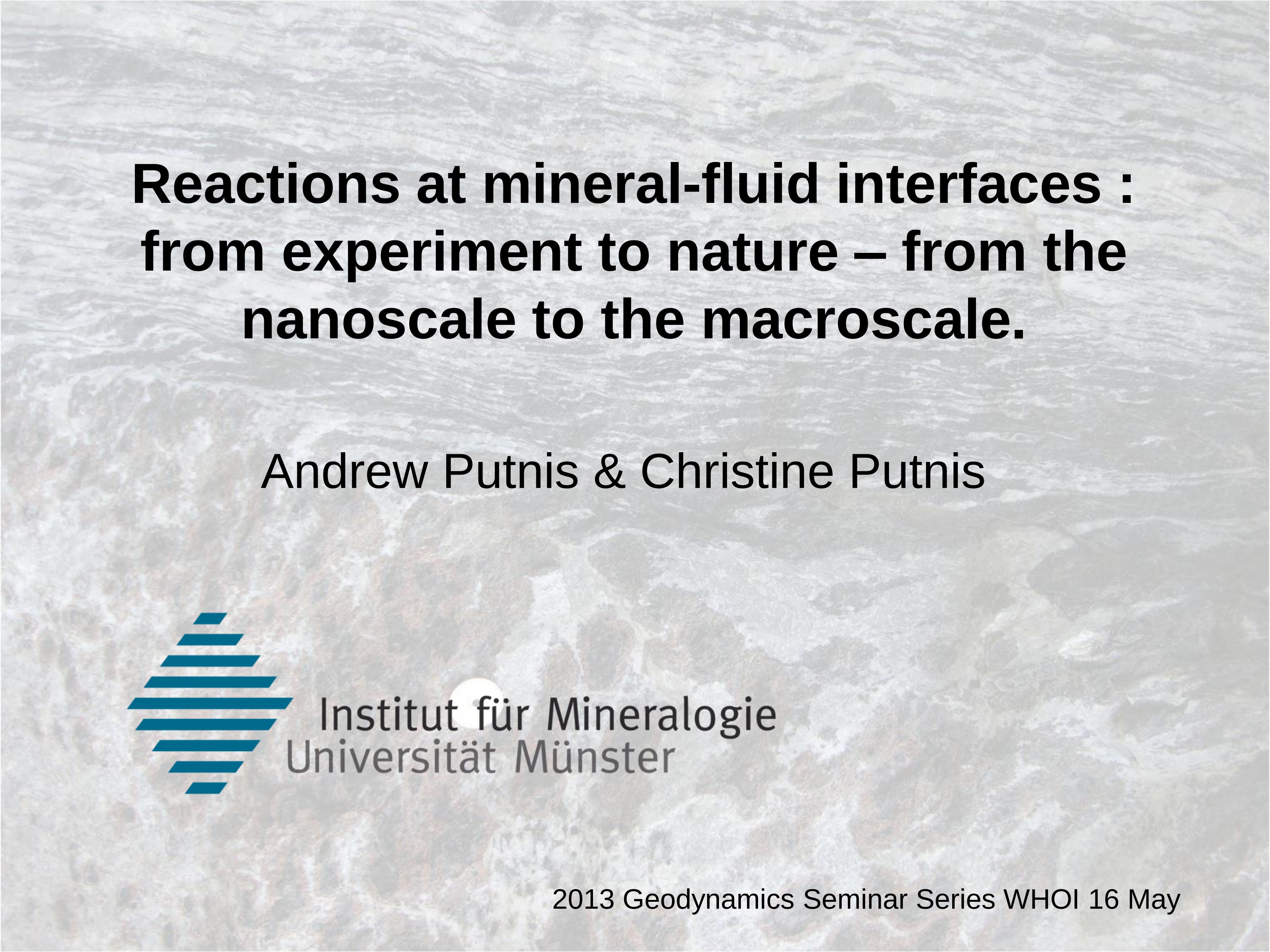


Reactions at mineral-fluid interfaces : from experiment to nature – from the nanoscale to the macroscale.

Andrew Putnis & Christine Putnis

Institut für Mineralogie
Universität Münster

2013 Geodynamics Seminar Series WHOI 16 May

The study of surfaces of crystalline solids:

Through most of the 20th century :

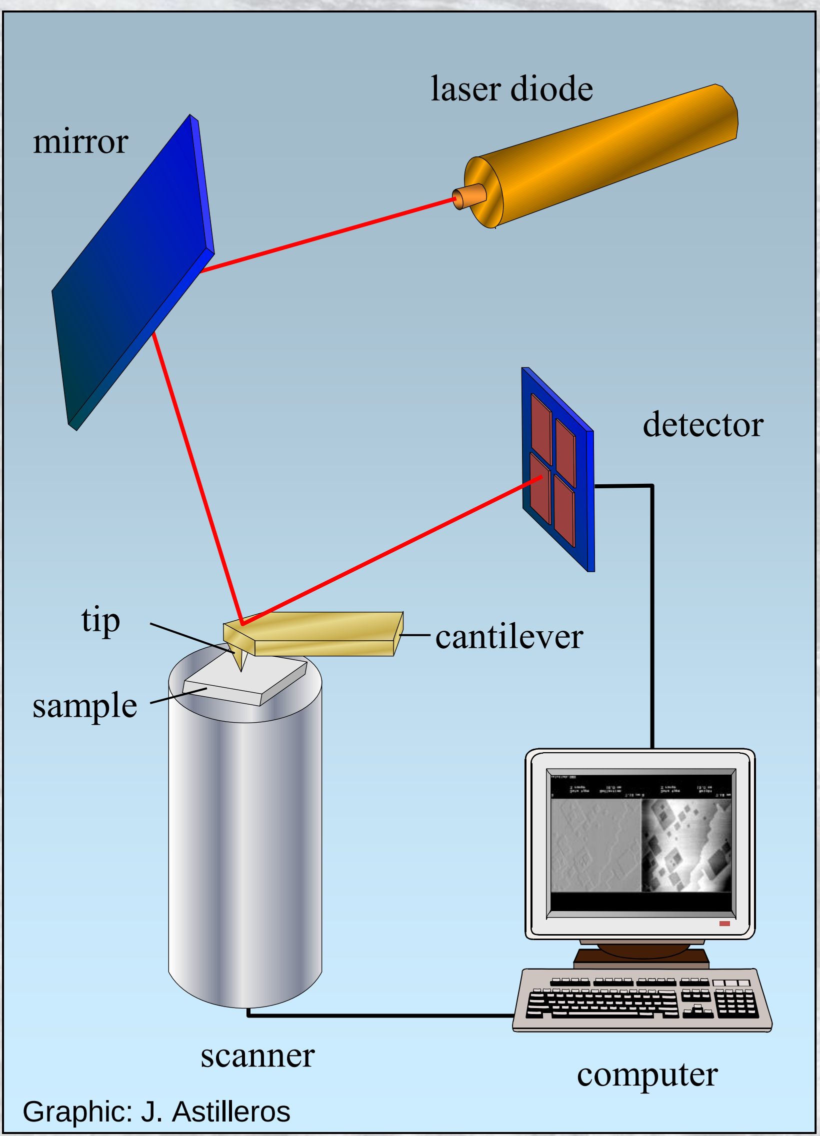
Essentially the preserve of physicists. Ultra-clean surfaces studied in high vacuum with various spectroscopic and diffraction methods (XPS, LEED…..)

1986: Invention of the Atomic Force Microscope (AFM) by Binnig, Quate & Gerber, a development from Scanning Tunnelling Microscopy (Binnig and Rohrer, Nobel Prize for Physics, 1986).

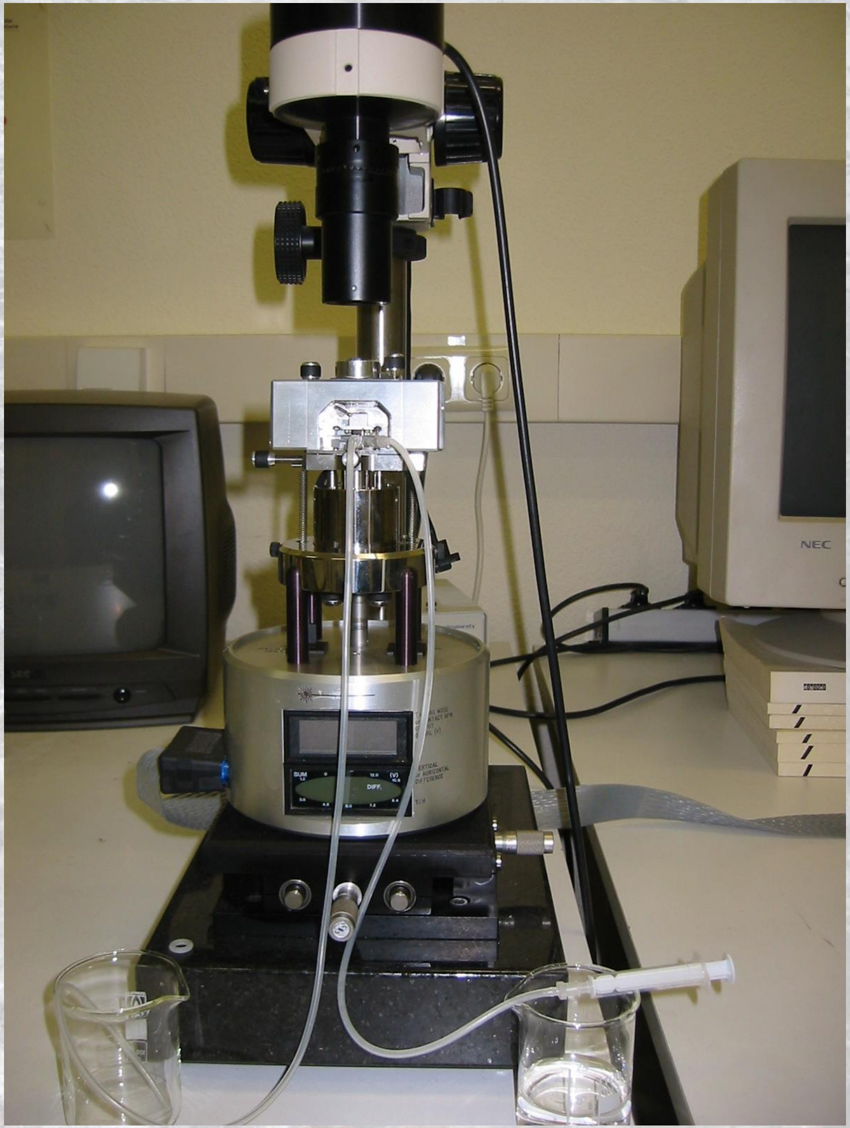
1989: First commercial AFM.

** Can image surfaces with sub-Ångstrom *z*-resolution *under fluid*.**

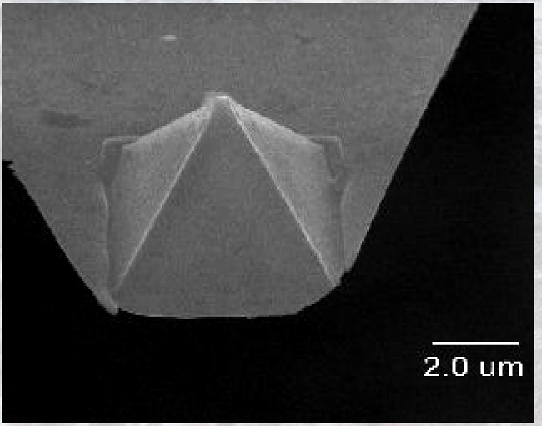
Atomic Force Microscopy

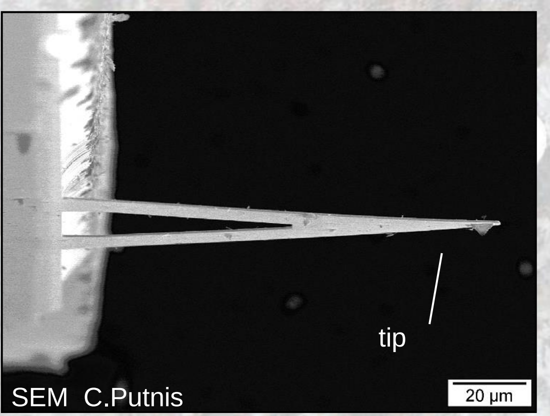


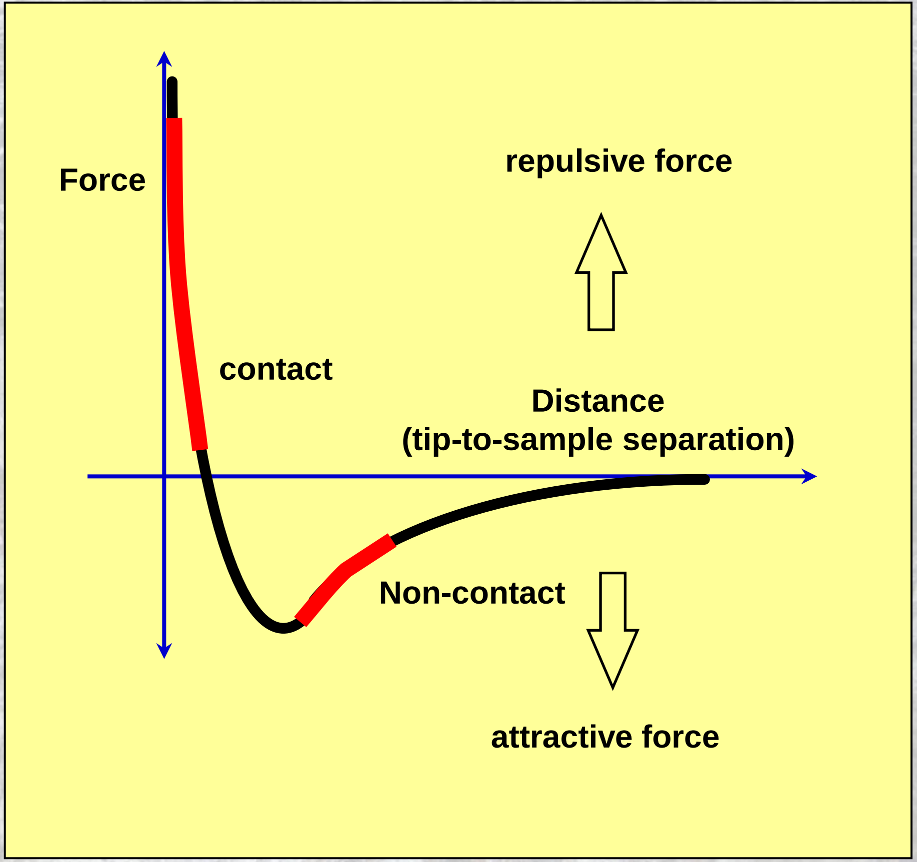
Graphic: J. Astilleros



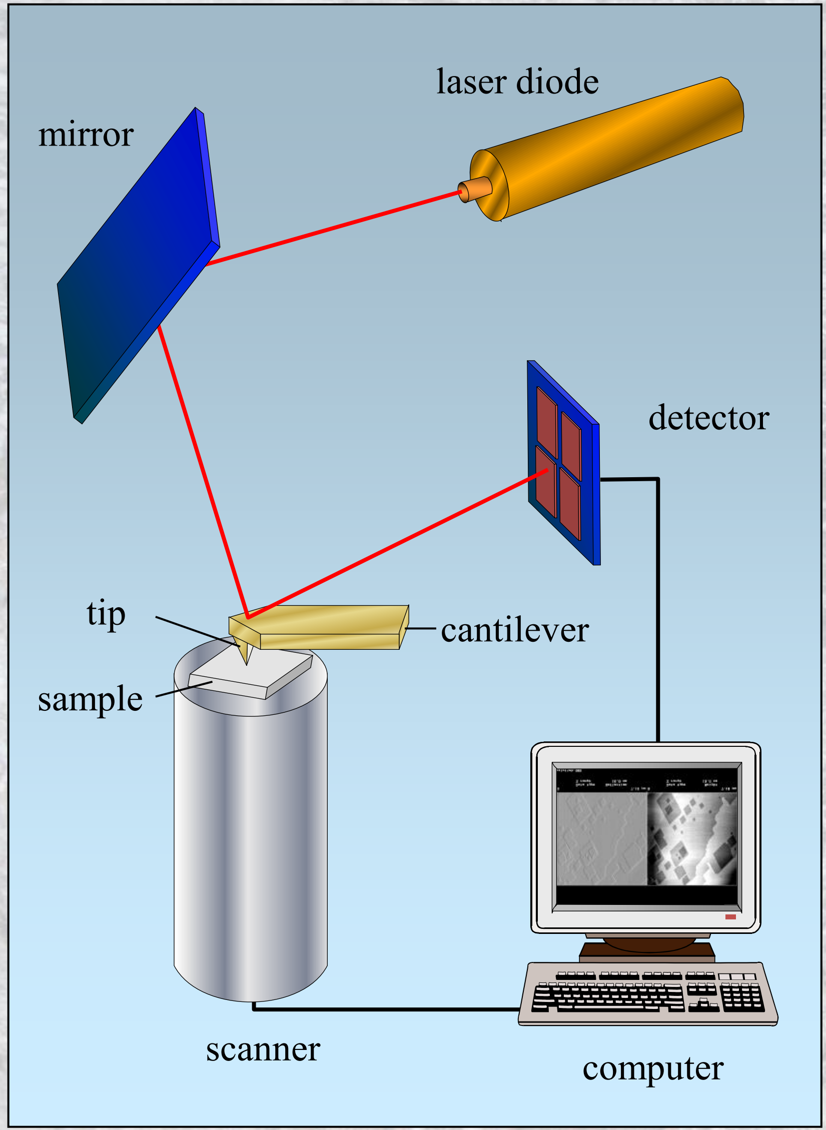
An Atomic Force Microscope (AFM) measures and images the interaction between a sharp tip and a mineral surface

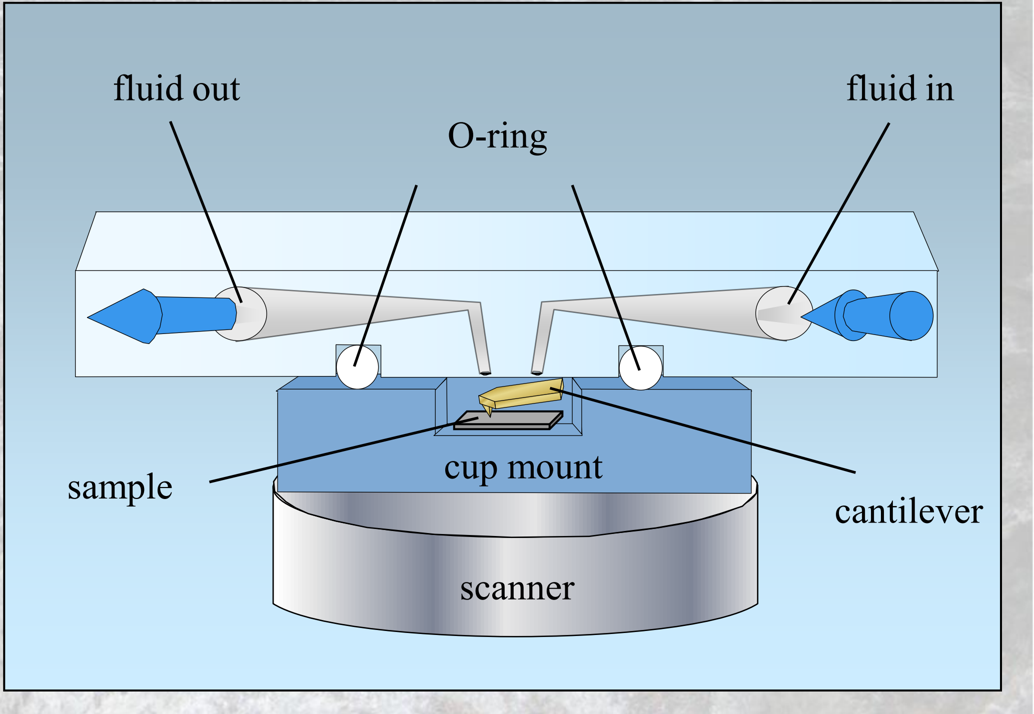






In situ crystal growth experiments in a fluid cell of an Atomic Force Microscope (AFM)





Graphic: J. Astilleros

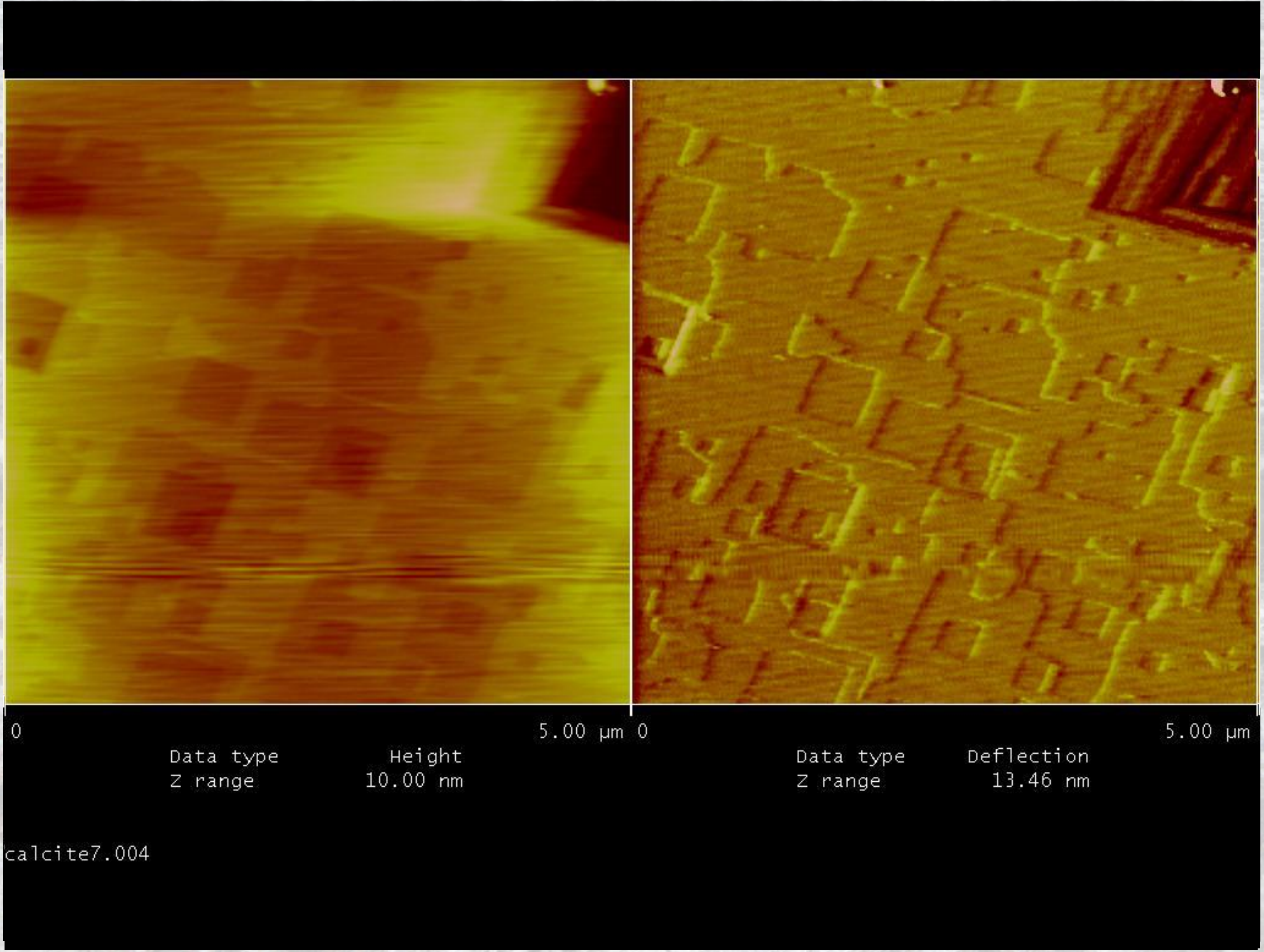
What can we do with an AFM?

- Direct *in situ* observations of the mechanisms of dissolution and growth of minerals* as a function of:

  under- and super-saturation,
  fluid composition (pH, ionic strength,
  background electrolytes, additives etc.

  temperature – hydrothermal AFM (difficult but
  possible.

Morphology of dissolution of calcite in water

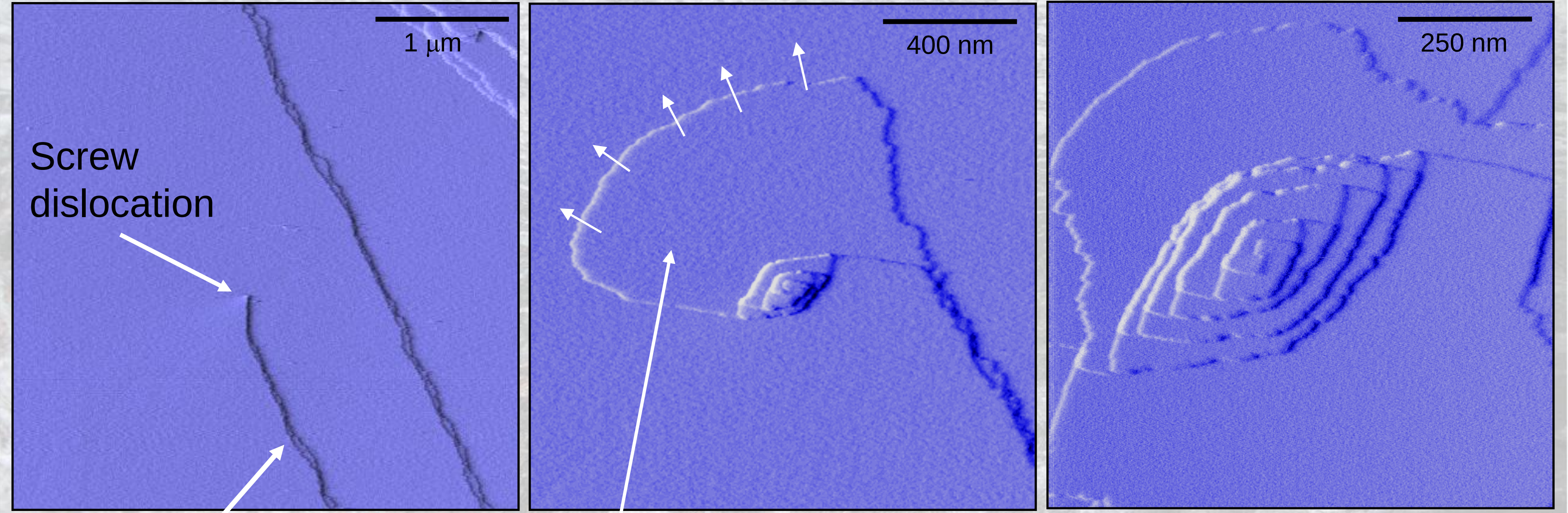


Mechanisms of dissolution are still not well understood:

- Reactivity of surfaces
- Anisotropy of reactivity of different crystallographic surfaces as well as spatial variations on a single surface (different surface sites)
- Dissolution involves hydration of ions – how does the dynamics of the water structure affect this?
- How do additives affect the water structure dynamics i.e. the difference between ‘bulk water’ and water around the additive.
- etc. etc.

Mechanisms of crystal growth:

Spiral growth and step advancement on (001) of barite, $BaSO_4$ from a supersaturated solution

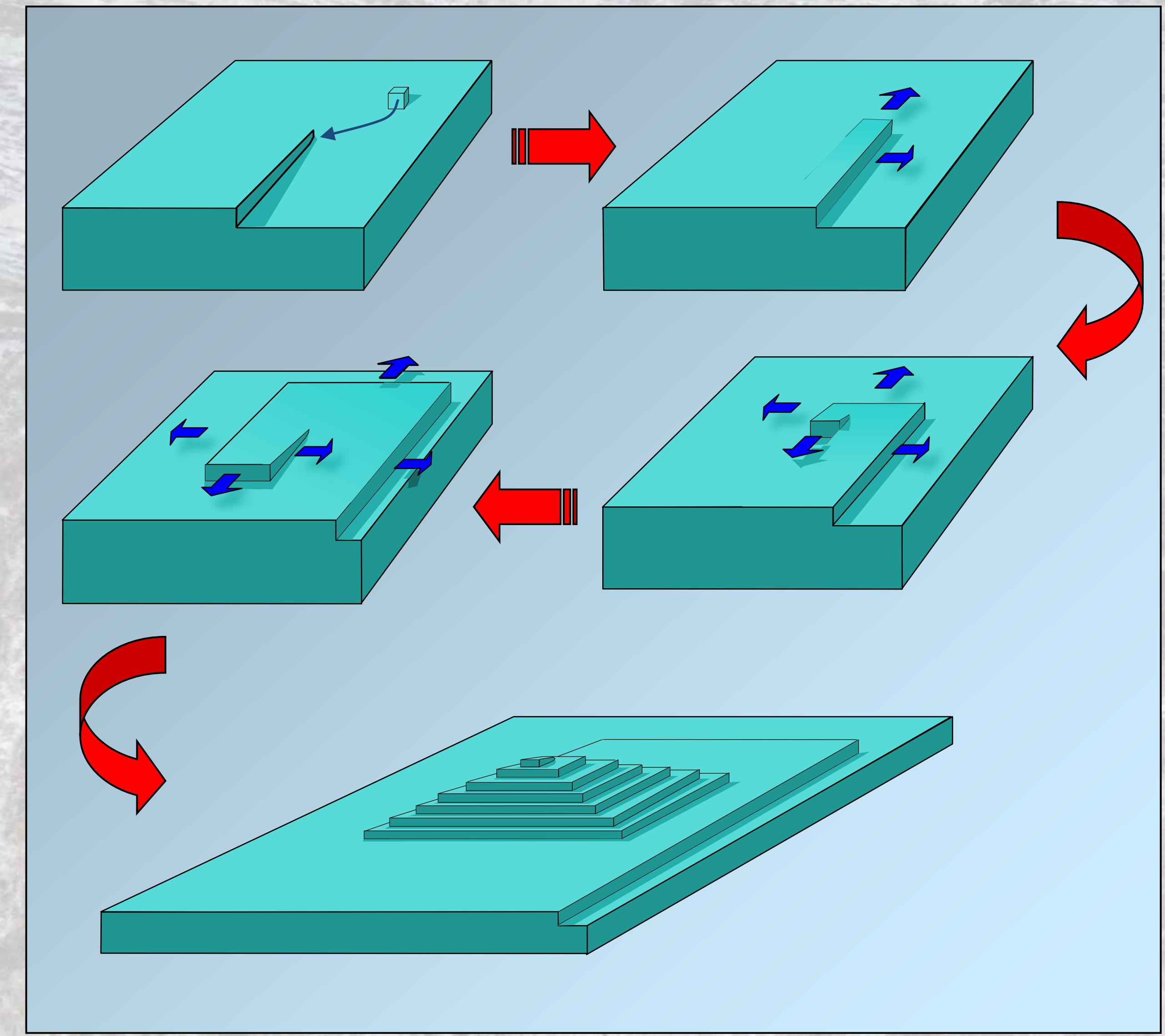


Screw dislocation

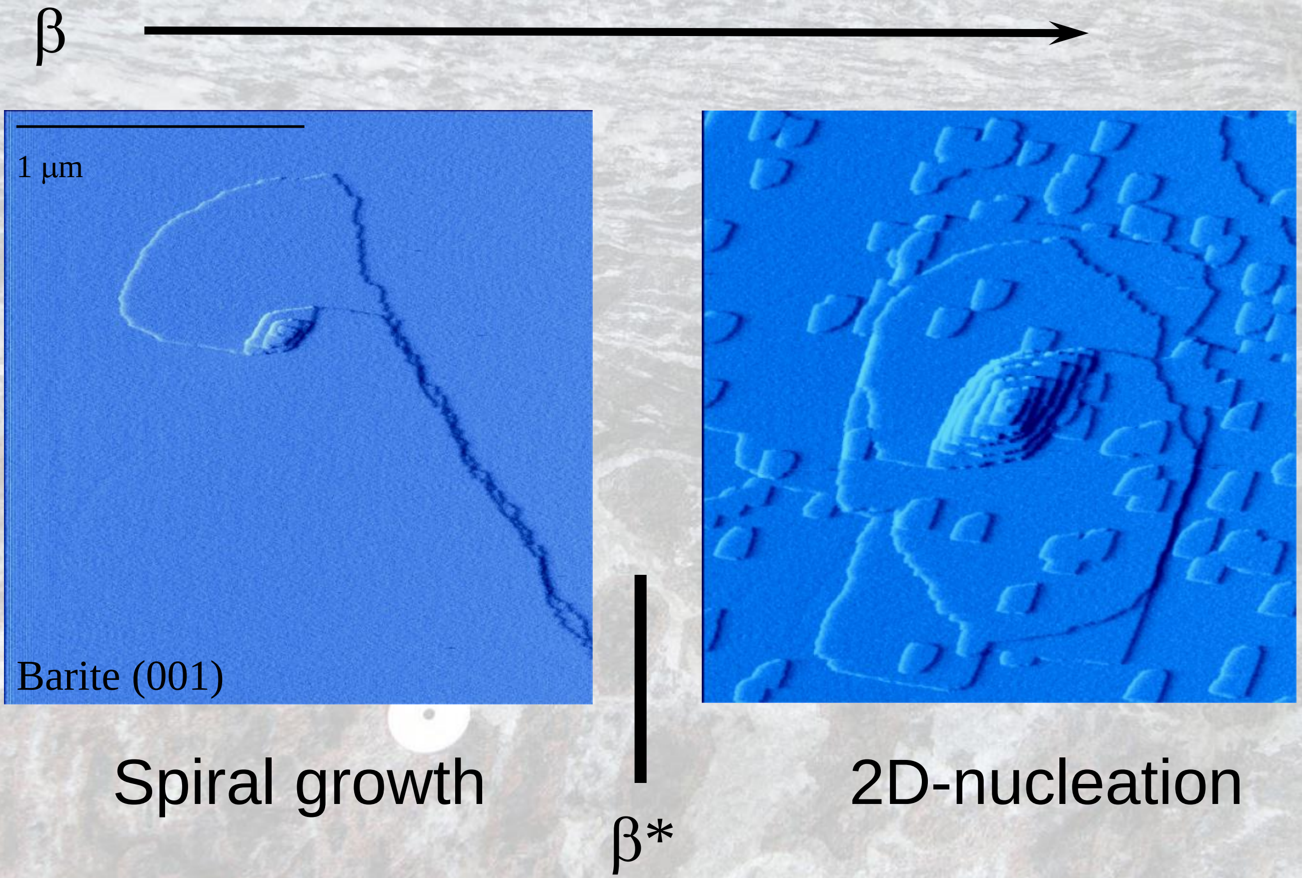
Cleavage step : 2 $BaSO_4$ layers

New growth step : 1 $BaSO_4$ layer, spreading anisotropically

Spiral growth around the core of a screw dislocation



Increasing supersaturation : from spiral growth to 2-D nucleation

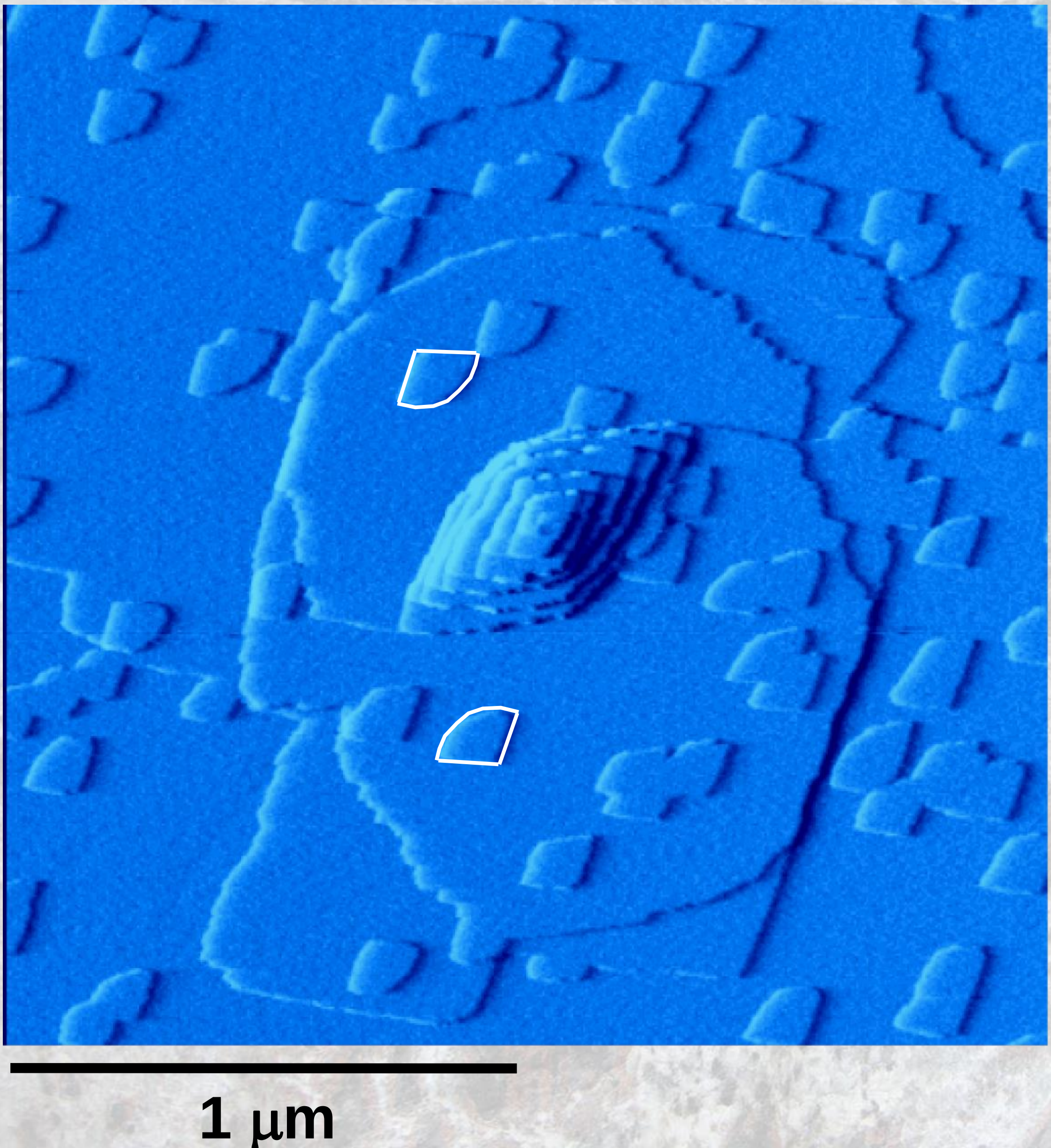


Spiral growth

β*

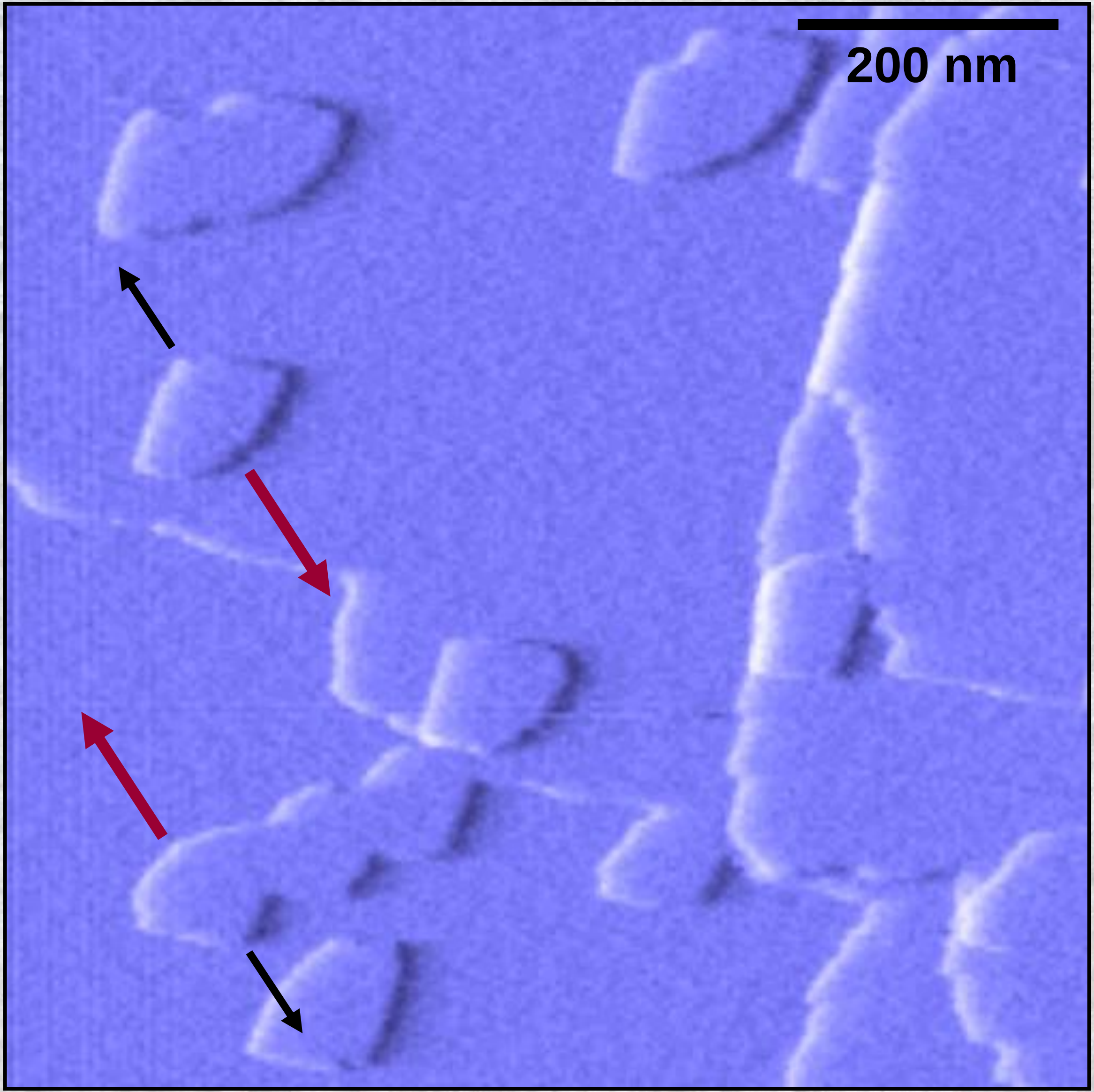
2D-nucleation

Island morphology



The shape and anisotropic growth of islands growing on the two different $BaSO_4$ layers are related by a 2_1 screw axis

Growth rate anisotropy of islands growing on (001) barite



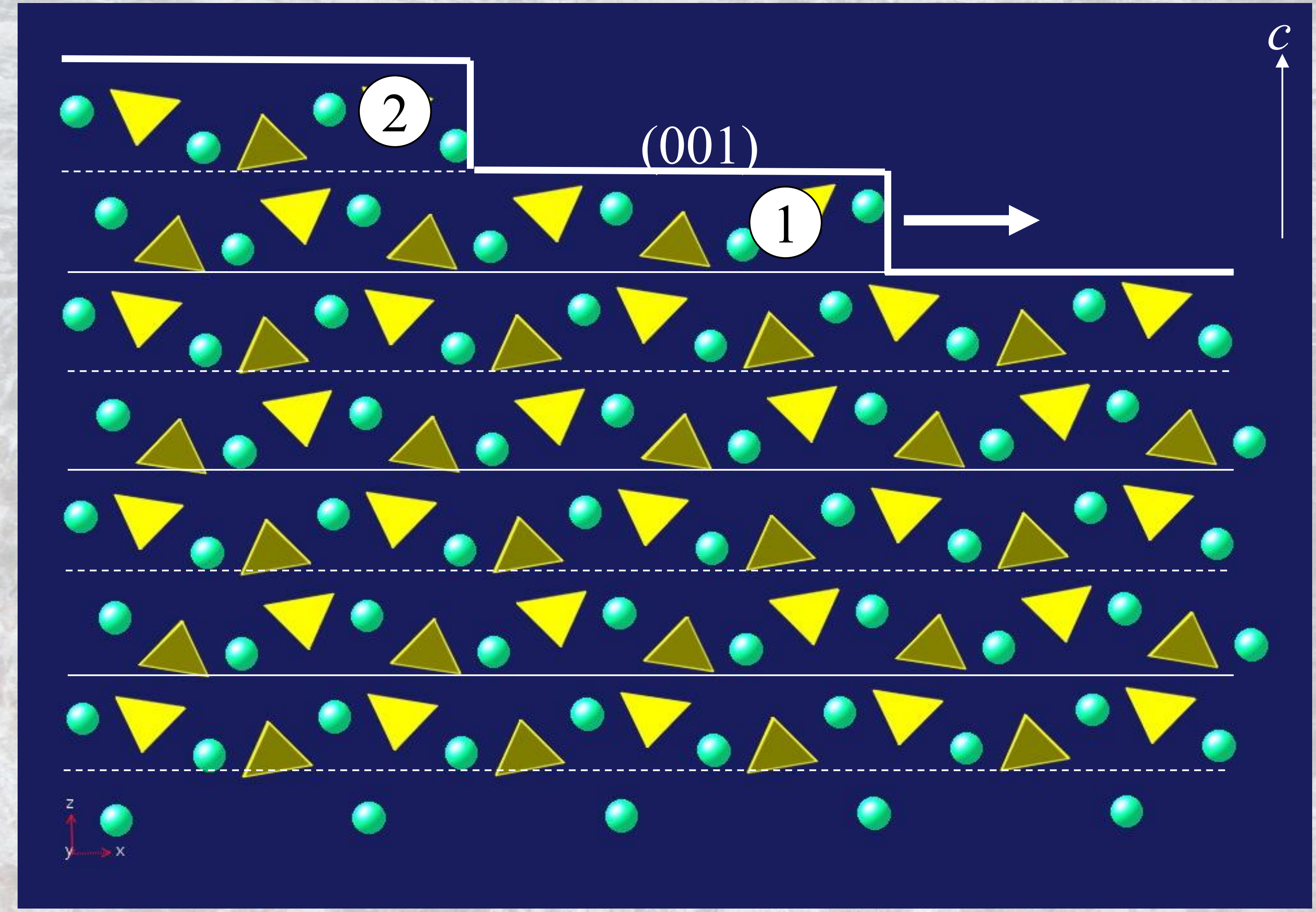
Growth rate in the direction shown by

↘ ↖

is ~ 10 times faster than in the direction shown by

↖ ↘

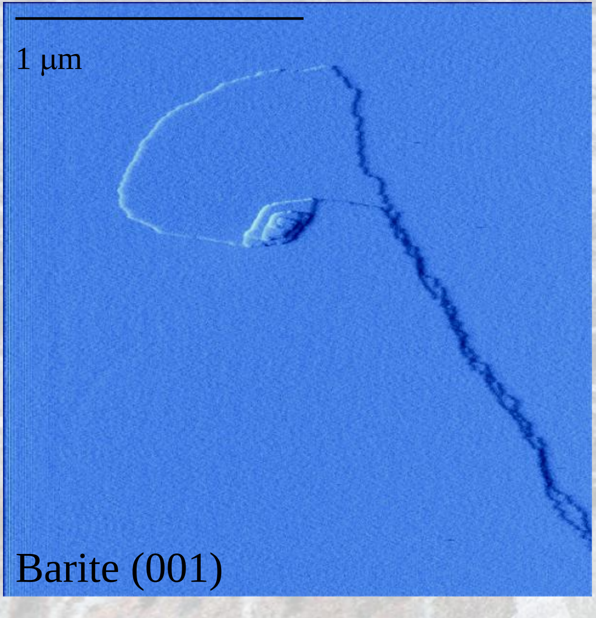
Growth (and dissolution) step on (001) barite - 1 $BaSO_4$ layer high



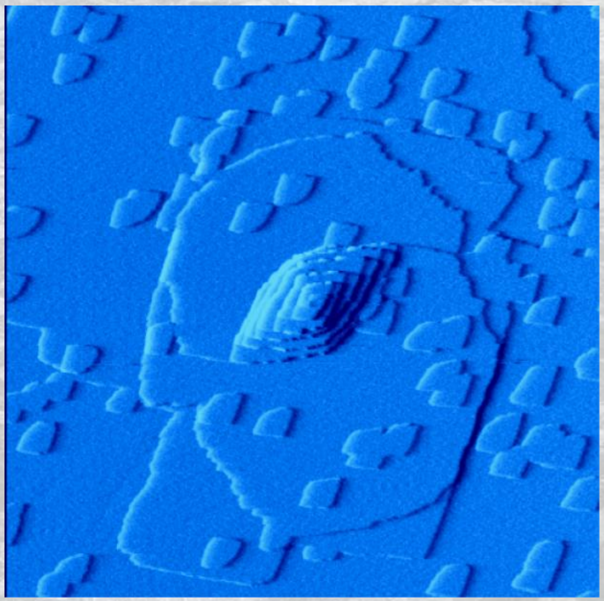
Different parts of the surface can have a different crystal structure.

Increasing supersaturation : from spiral growth to 2-D nucleation

$\beta \longrightarrow$



Spiral growth

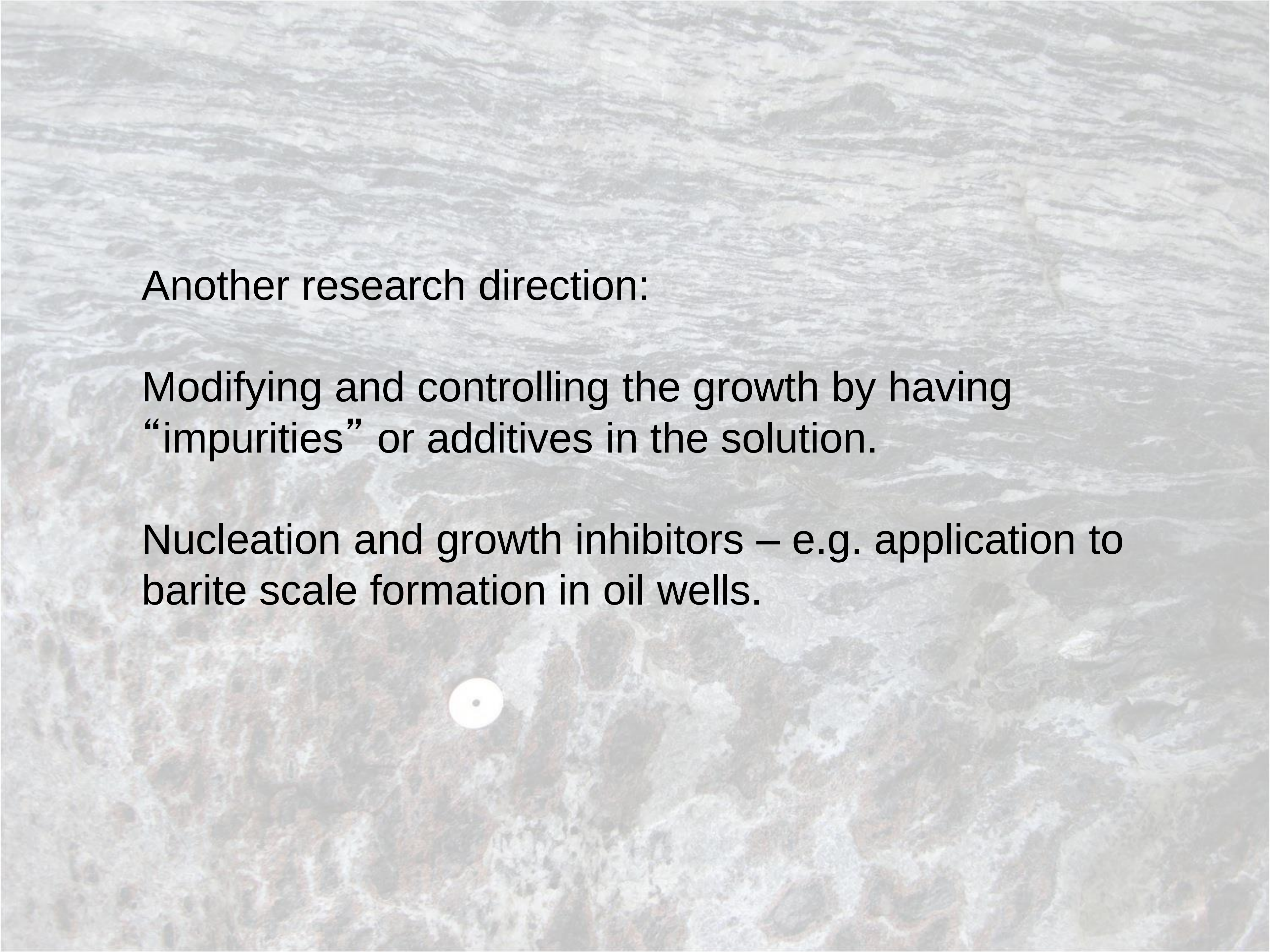


2D-nucleation

β^*

β^* is the threshold supersaturation for the onset of 2-D nucleation. We can determine this for different end-member compositions of solid solutions e.g. $BaSO_4$, $SrSO_4$ …

This leads to the problem of how solid solutions grow from multicomponent aqueous solutions.

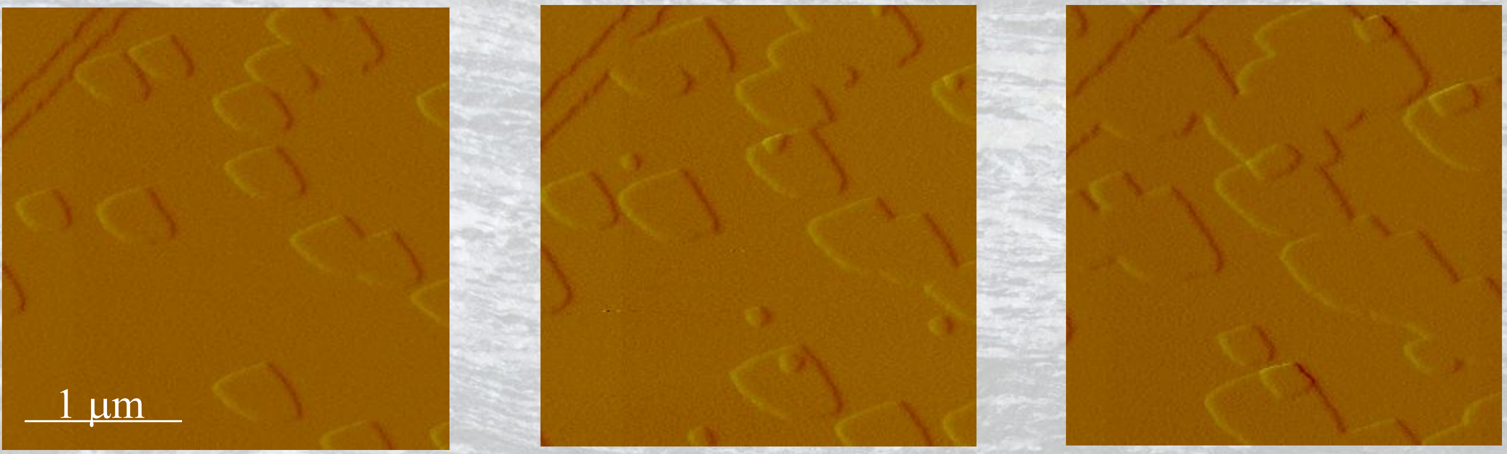


Another research direction:

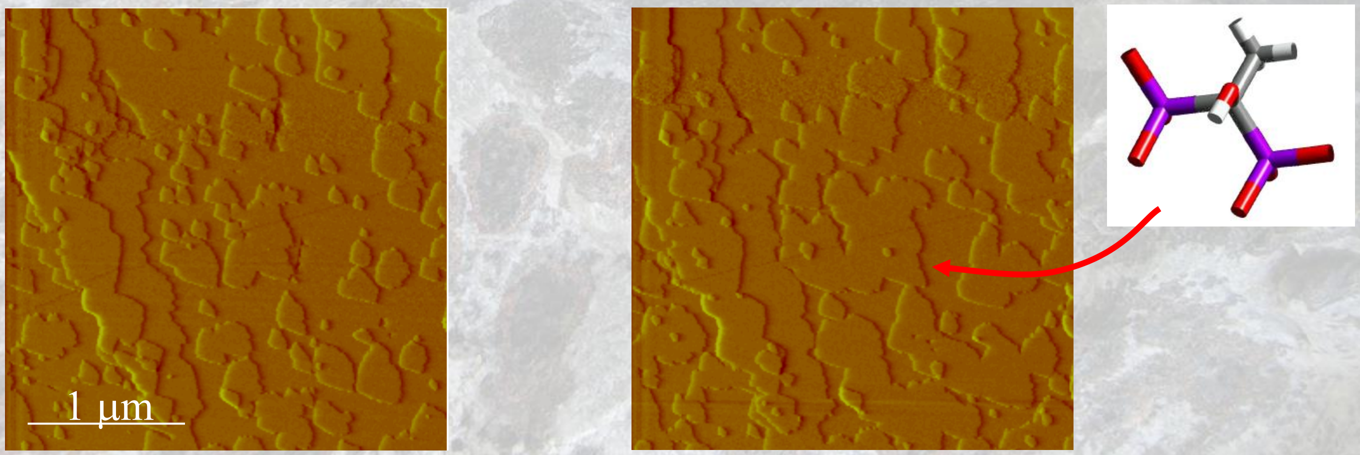
Modifying and controlling the growth by having “impurities” or additives in the solution.

Nucleation and growth inhibitors – e.g. application to barite scale formation in oil wells.

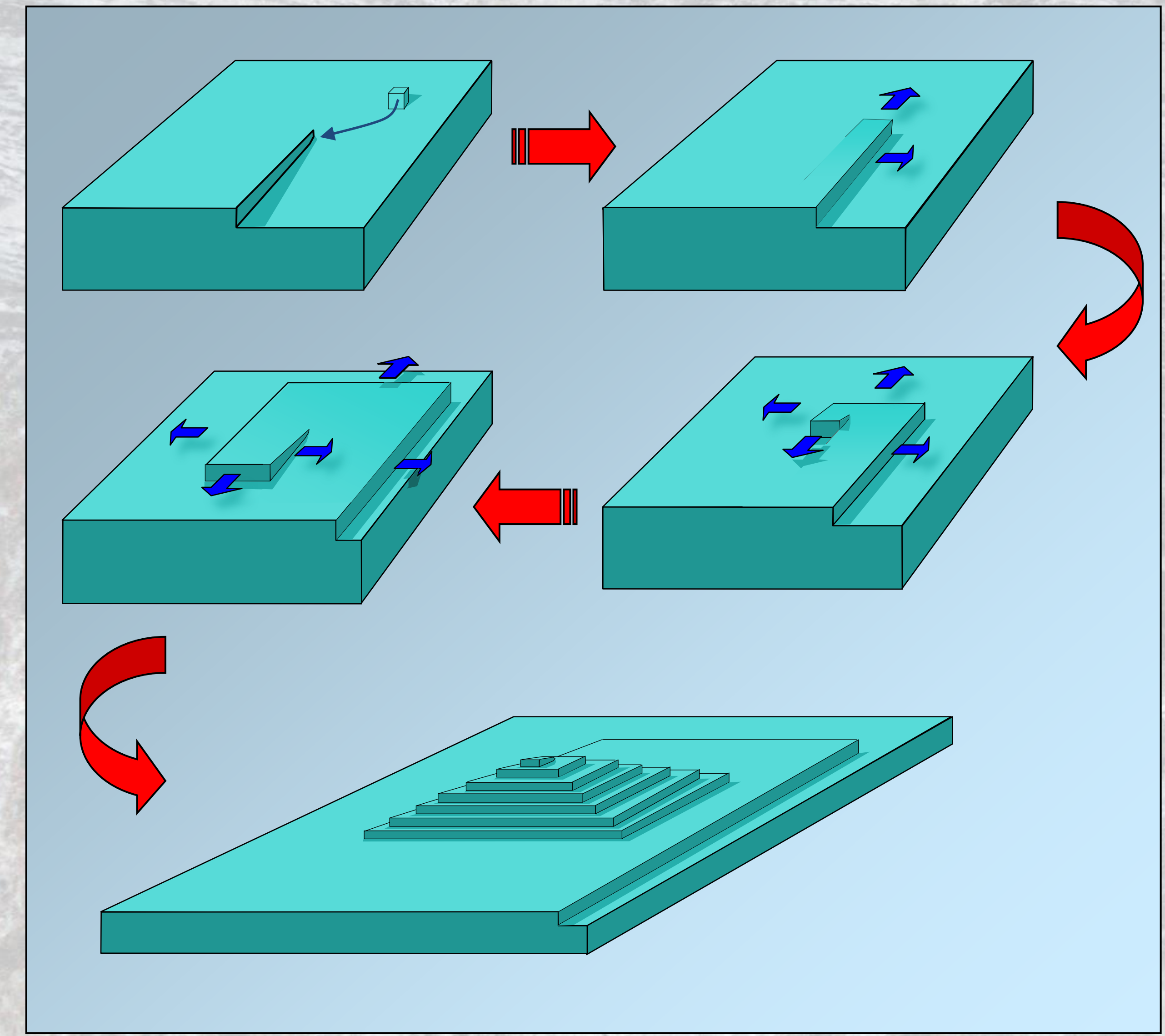
Pure barite growth sequence



Barite growth with HEDP ($C_2H_8O_7P_2$)



Spiral growth around the core of a screw dislocation

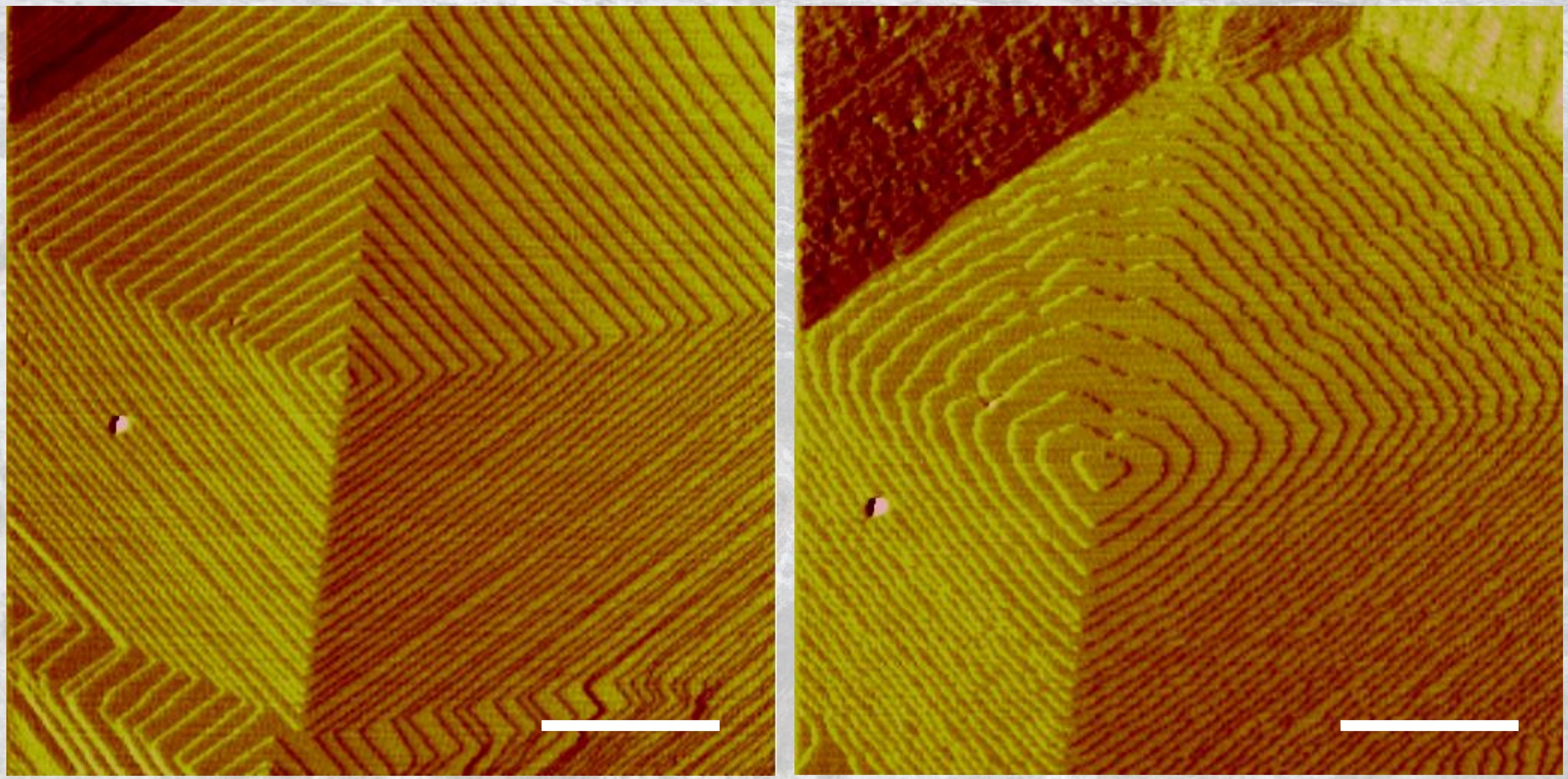


Spiral growth hillocks on a calcite surface

from

(a) a pure supersaturated solution, and

(b) From a solution at the same supersaturation but with 60ppm Se



Renard et al., Chem. Geol. 2013 (In press)

What is “incongruent dissolution” and what is the mechanism?

e.g. 1. Dissolution of dolomite Ca,Mg$(CO_3)_2$

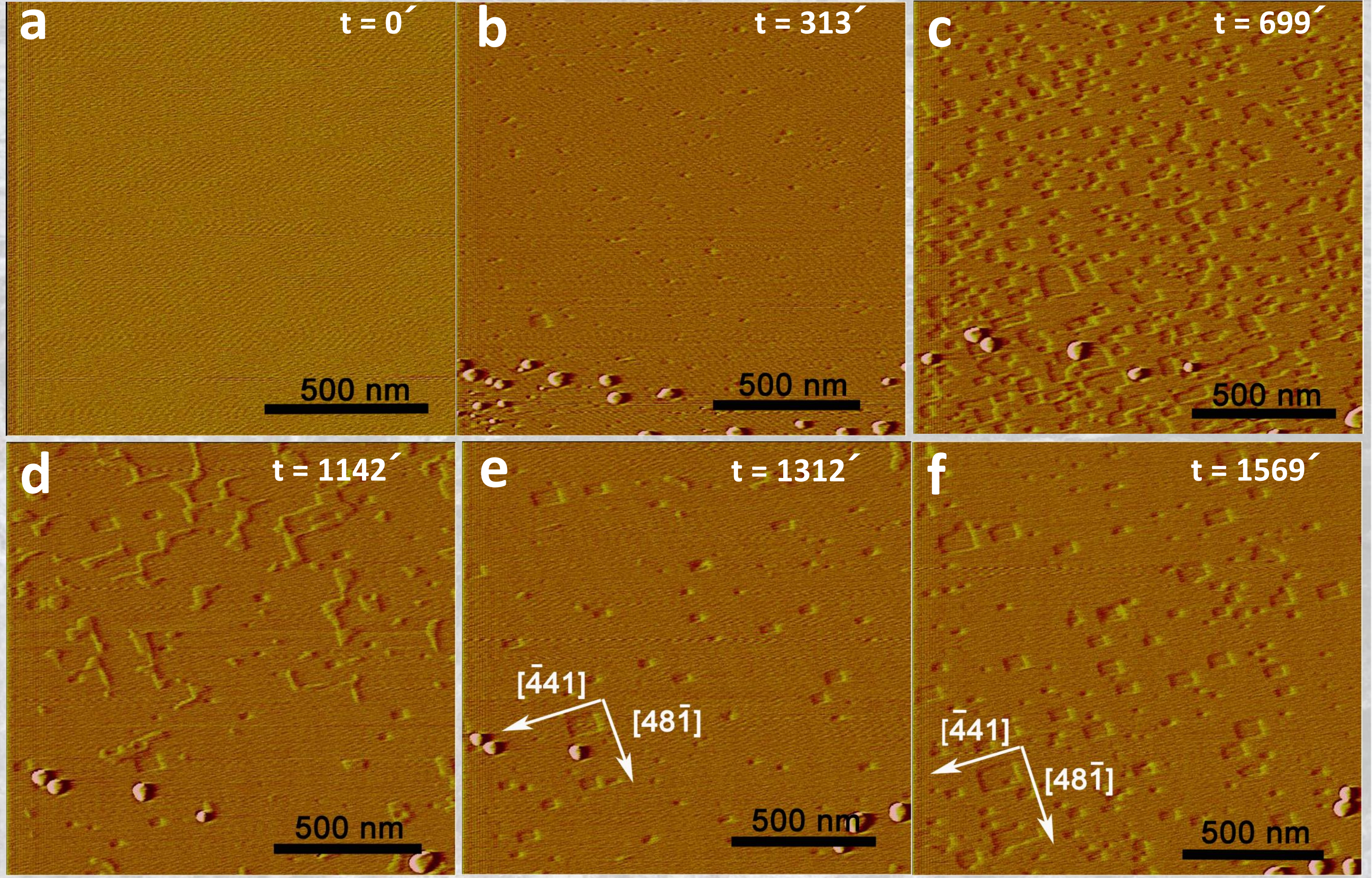
Release rate of Ca is apparently greater than that of Mg, leaving an Mg-enriched layer on the surface

e.g. 2. Dissolution of wollastonite $CaSiO_3$

Release rate of Ca greater than Si, leaving an Si-enriched layer on the surface

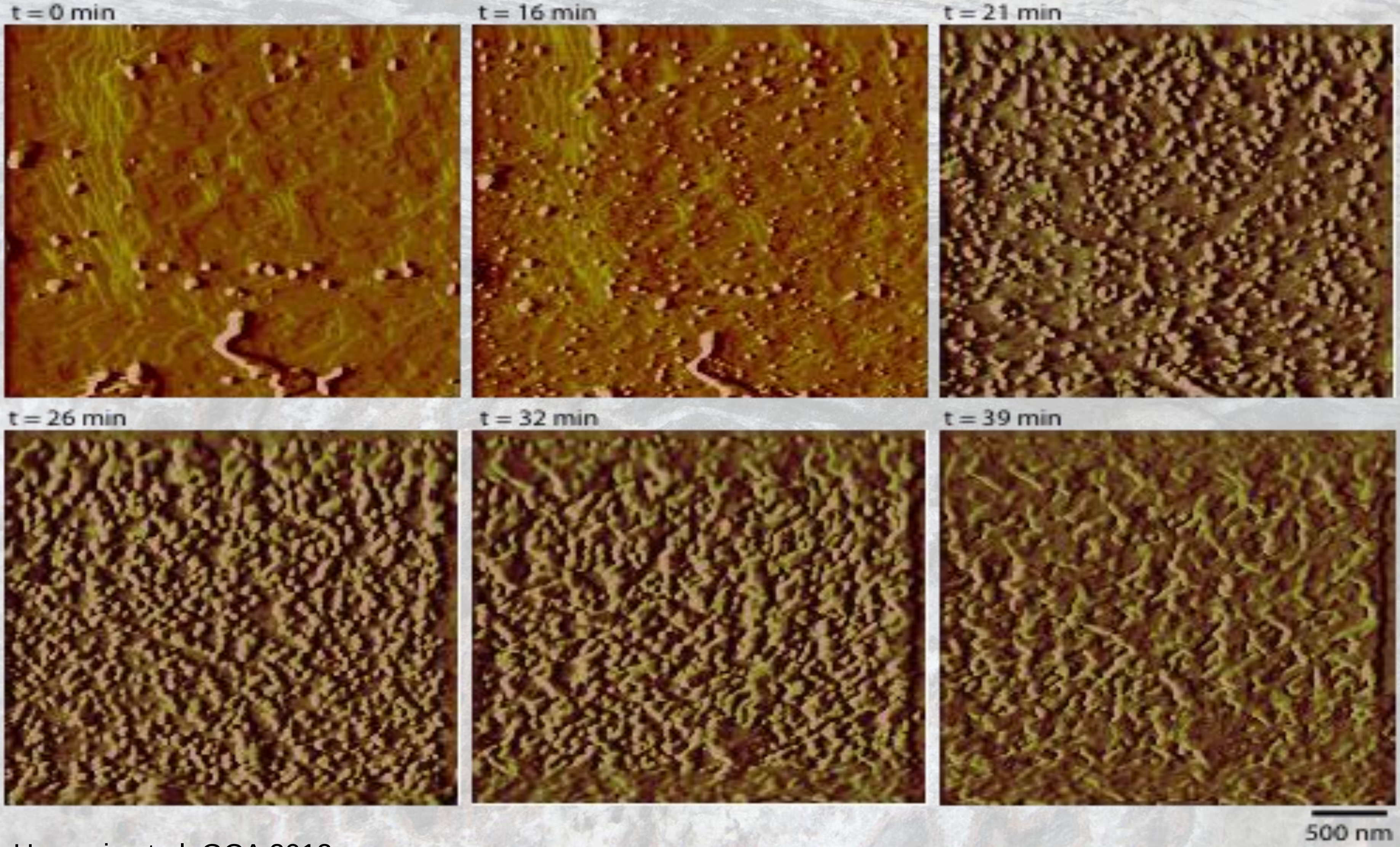
“Leaching” – a general description of “selective dissolution”

In situ AFM observations of dolomite dissolution (pH 7)



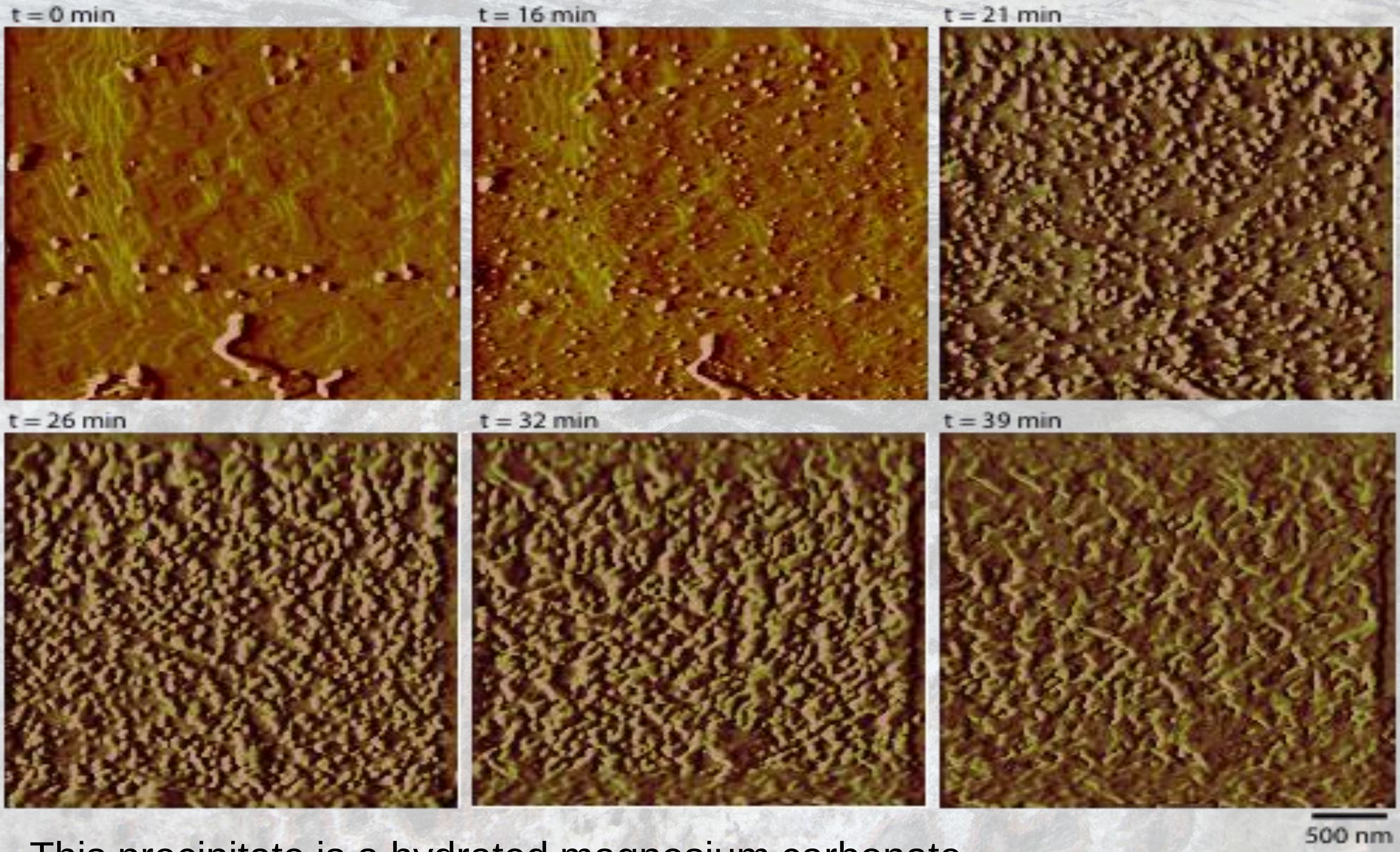
Urosevic et al. GCA 2012

In situ AFM observations of dolomite dissolution (pH 3)



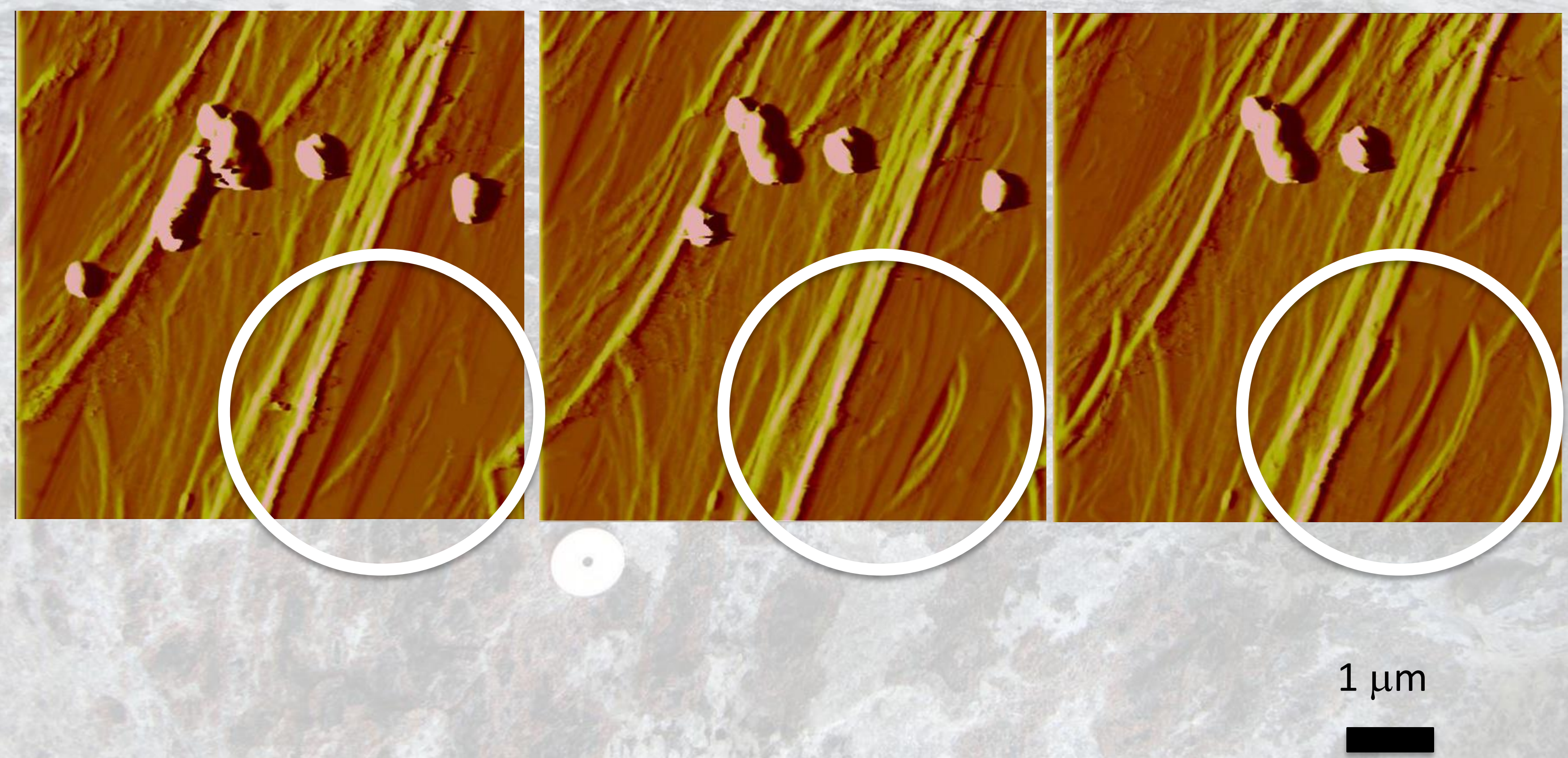
Urosevic et al. GCA 2012

The dissolution of dolomite is accompanied (coupled to) the precipitation of a new phase.



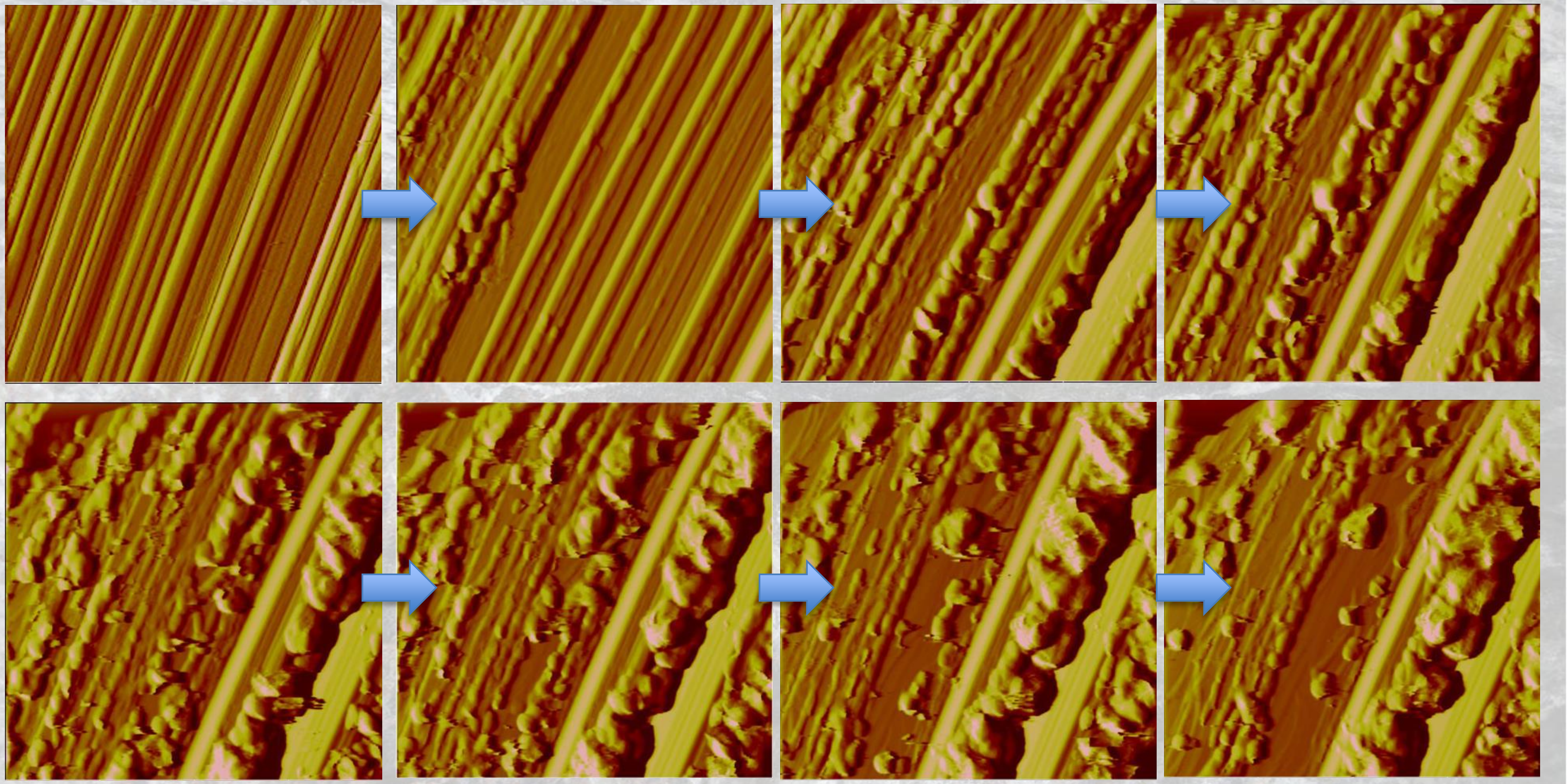
This precipitate is a hydrated magnesium carbonate.

In situ AFM observations of wollastonite $CaSiO_3$ dissolution



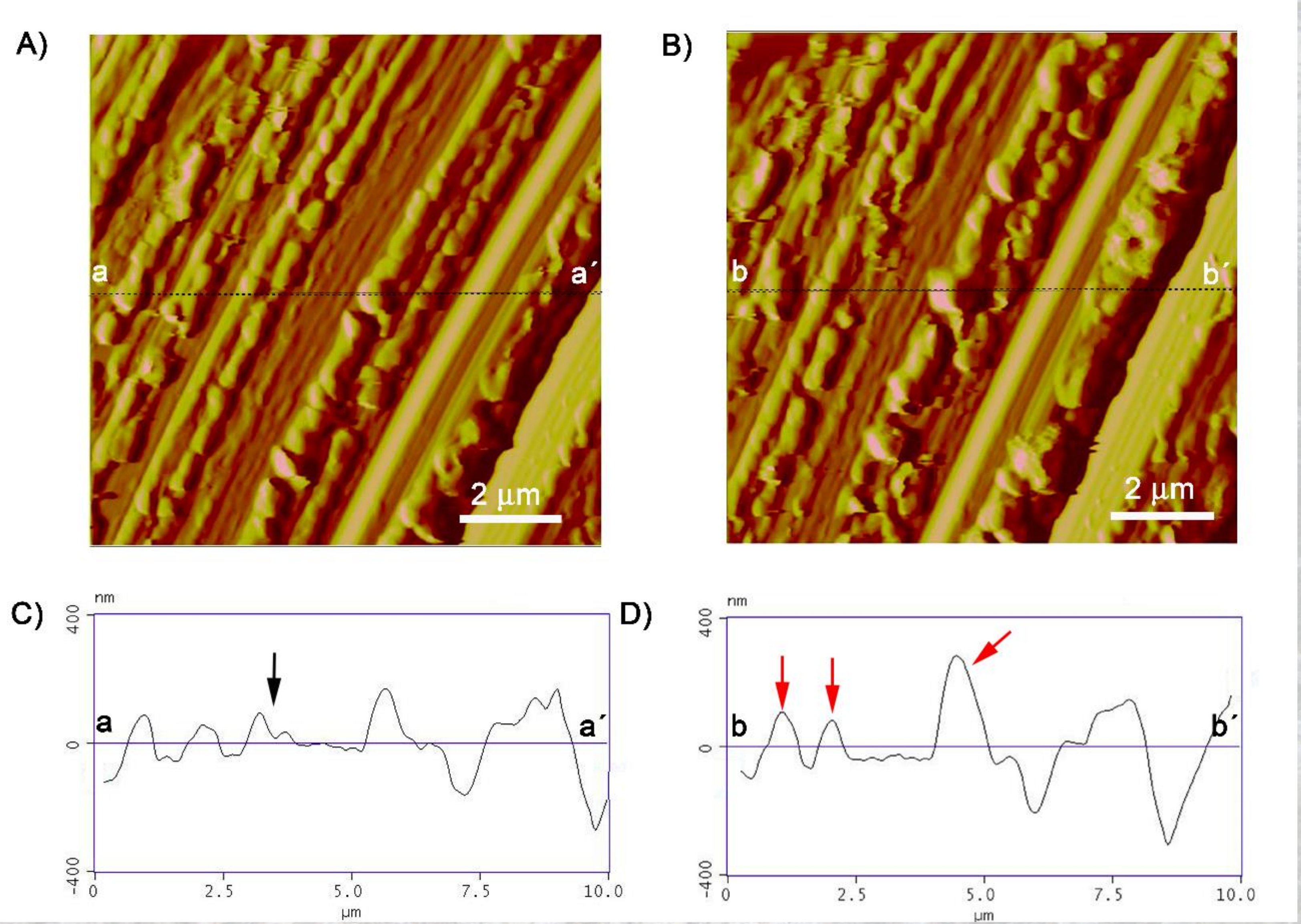
Ruiz-Agudo et al. GEOLOGY 2012

In situ AFM observations of wollastonite dissolution

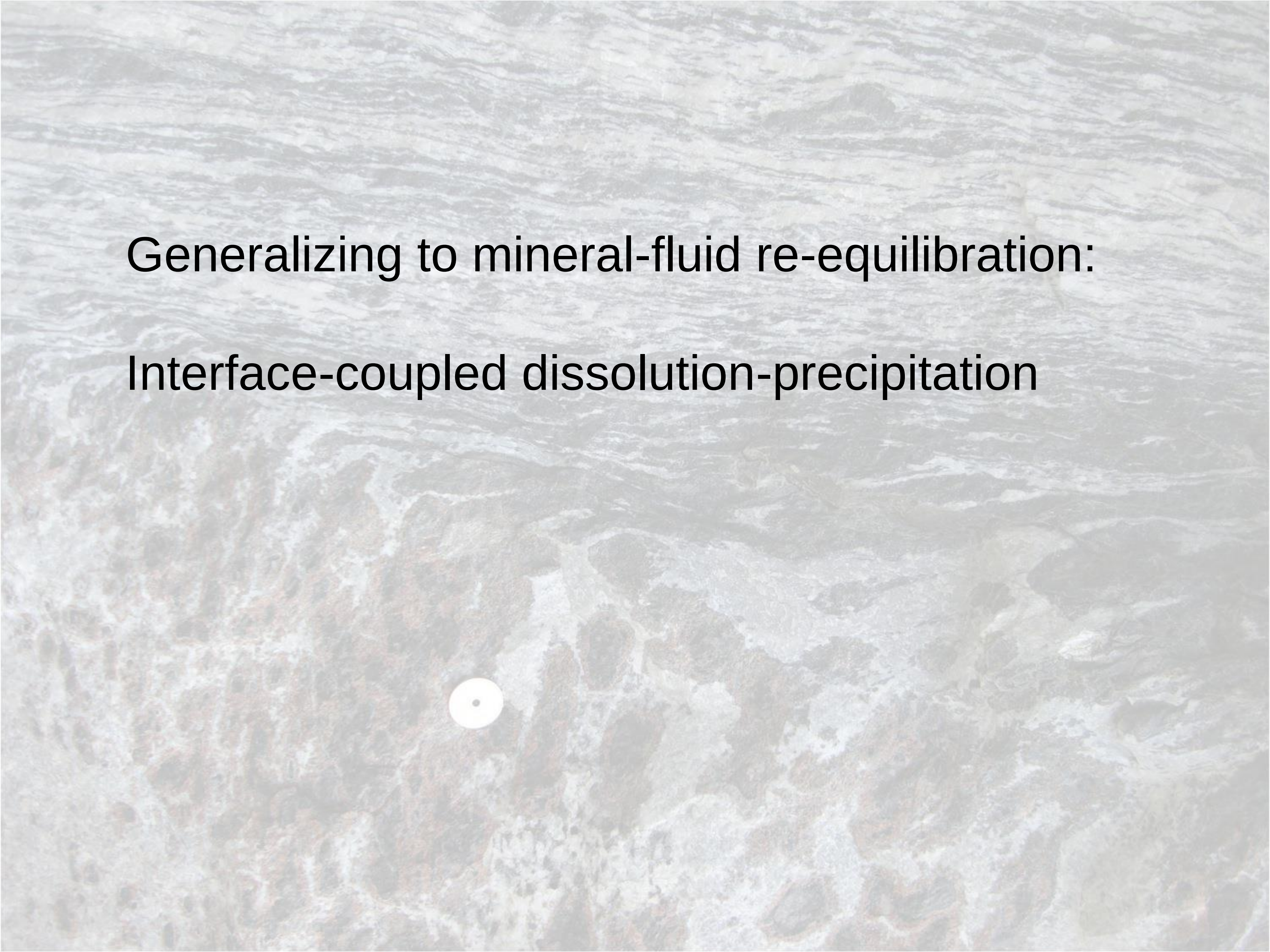


Ruiz-Agudo et al. GEOLOGY 2012

In situ AFM observations of wollastonite dissolution



Ruiz-Agudo et al. GEOLOGY 2012



Generalizing to mineral-fluid re-equilibration:

Interface-coupled dissolution-precipitation

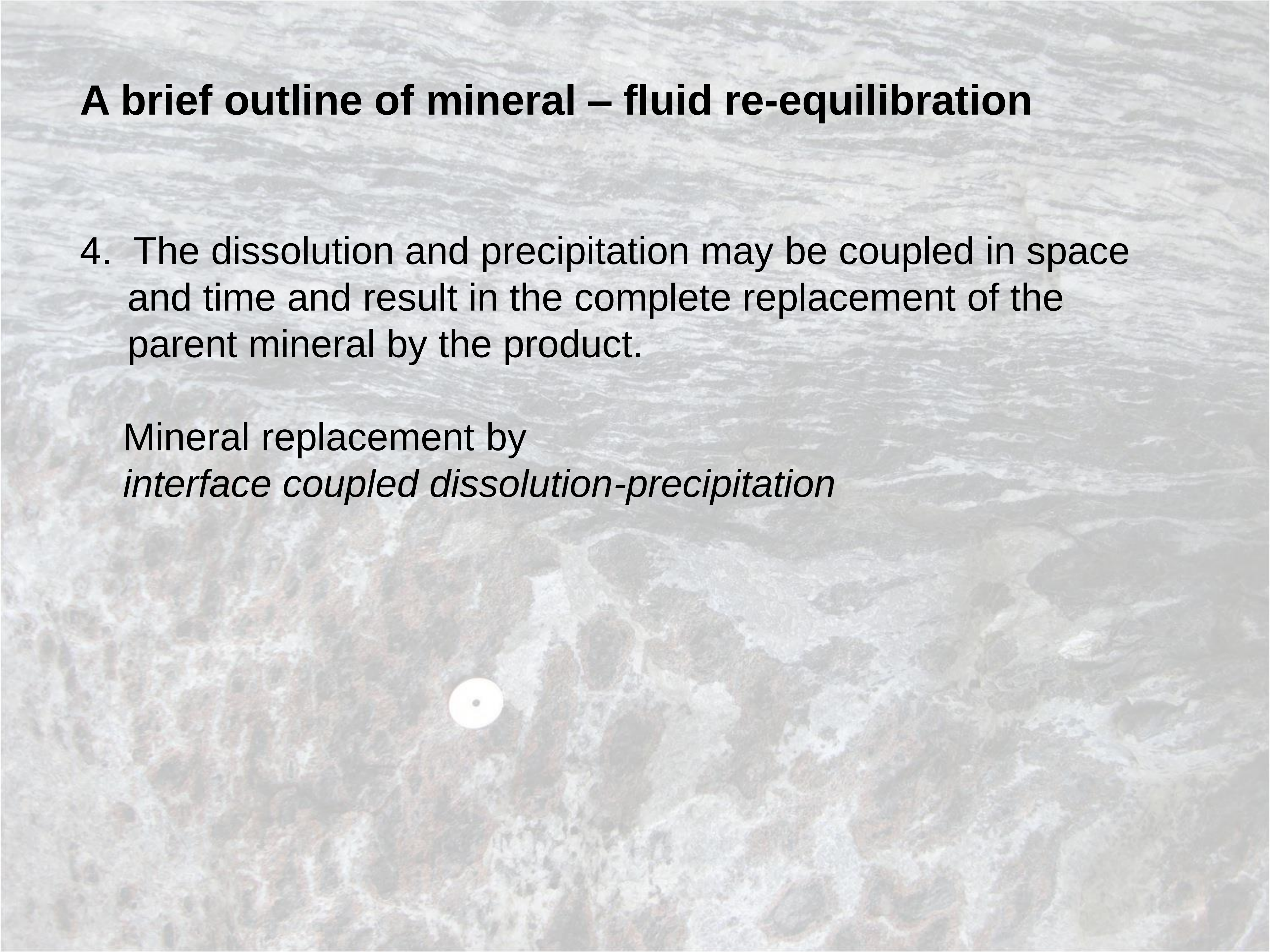
A brief outline of mineral – fluid re-equilibration

1. When a fluid interacts with a mineral phase with which it is out of equilibrium it will tend to dissolve the mineral.

   In a trivial case e.g. calcite-water, the mineral will continue to dissolve until the fluid reaches saturation

2. However, depending on the fluid composition, dissolution of the parent mineral may result in an interfacial fluid composition which is supersaturated with respect to another phase.

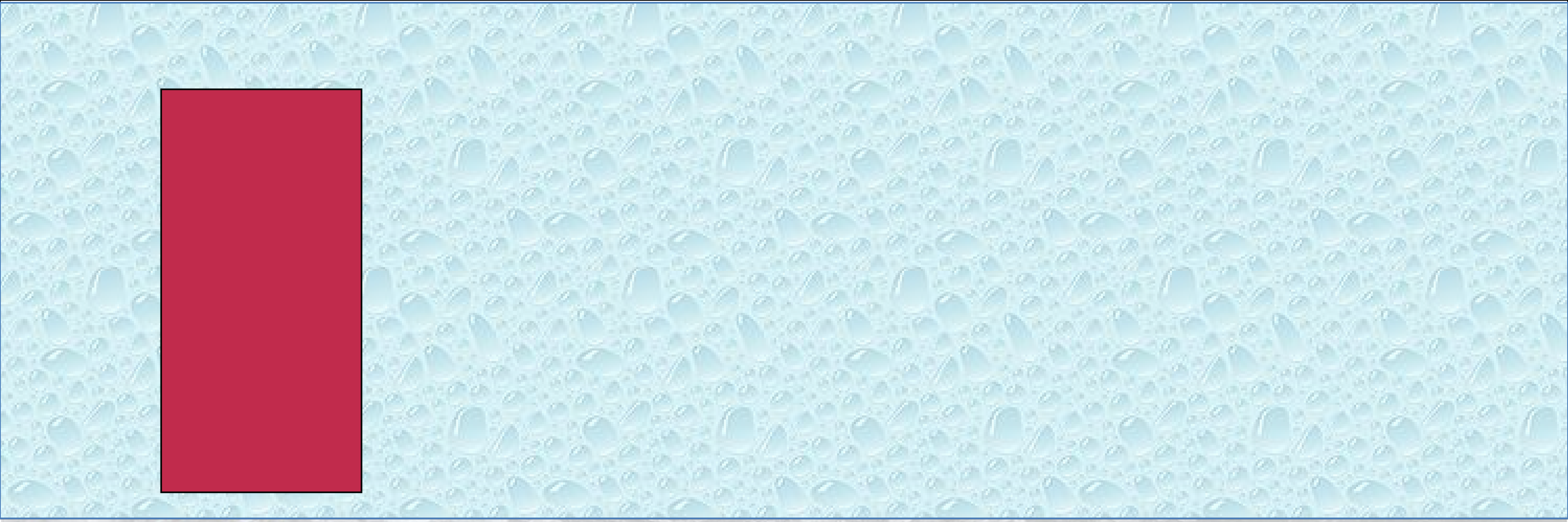
3. This product phase may nucleate within this interfacial fluid.



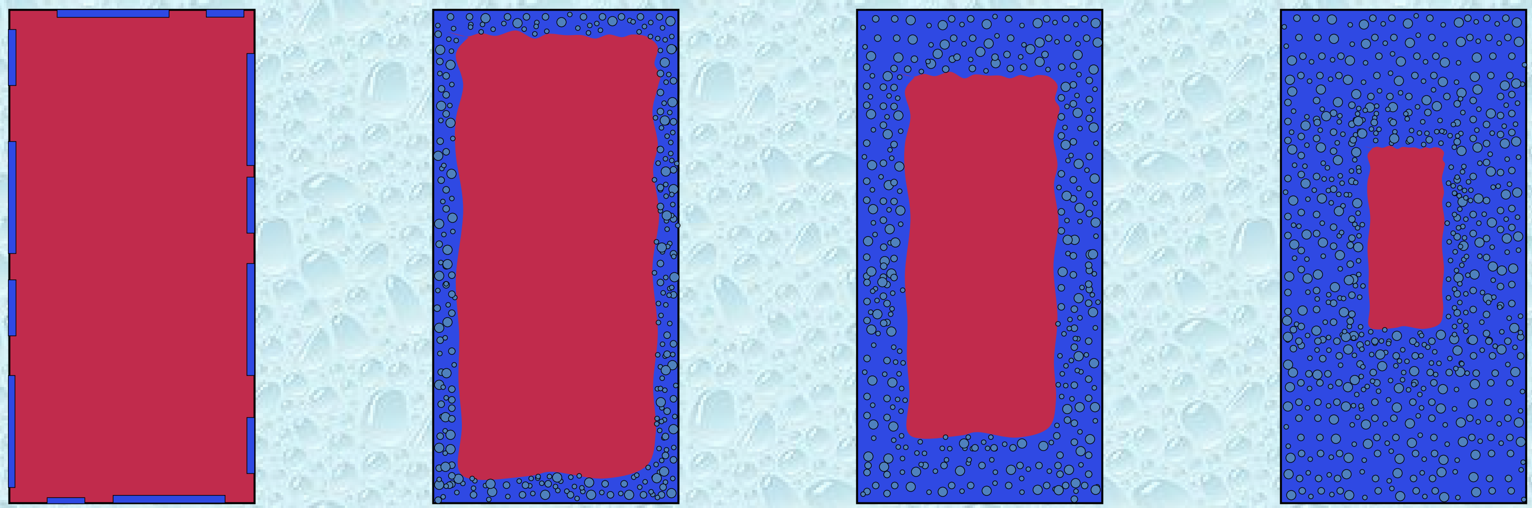
A brief outline of mineral – fluid re-equilibration

4. The dissolution and precipitation may be coupled in space and time and result in the complete replacement of the parent mineral by the product.

Mineral replacement by
interface coupled dissolution-precipitation



1. Dissolution of even a few monolayers of the parent surface results in a fluid boundary layer which is supersaturated with respect to a product phase.

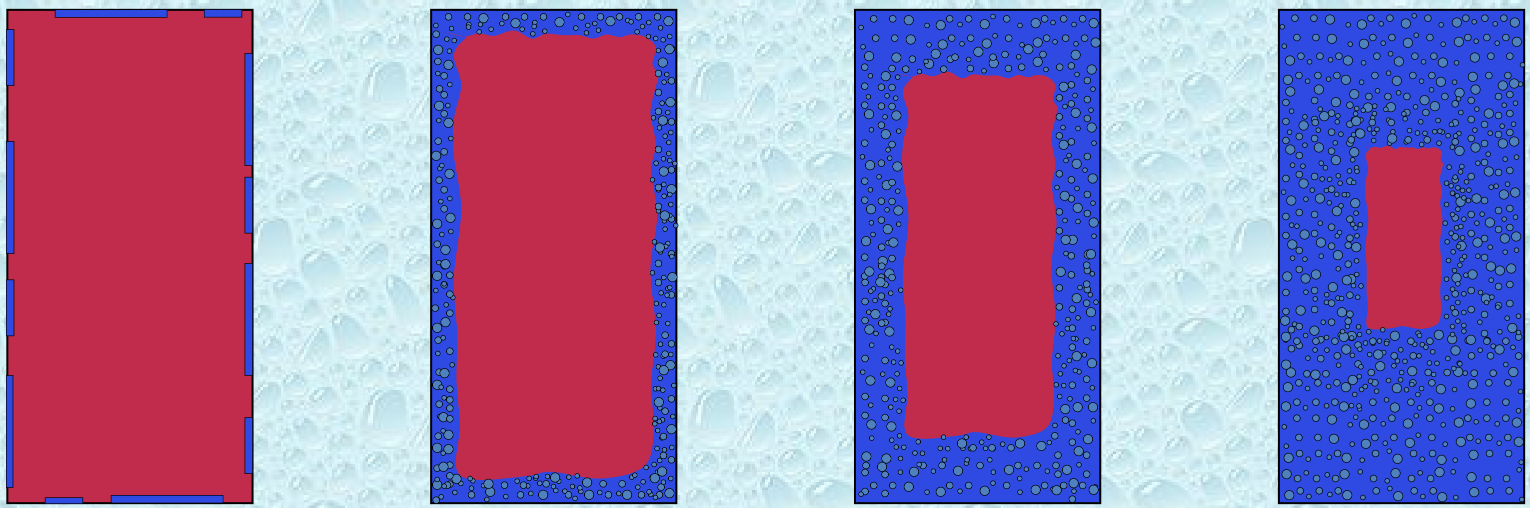


1. Dissolution of even a few monolayers of the parent surface results in a fluid boundary layer which is supersaturated with respect to a product phase.

2. Nucleation of the product on the parent surface depends on the degree of epitaxy between them.

3. Relative solubilities of parent and product in the fluid, and molar volume differences, define the porosity in the product

4. The reaction interface may then move through the parent phase.



- The external volume is preserved : differences in molar volume and relative solubility are taken into account by the porosity.
- The porosity itself constitutes a transient microstructure defined by the relationship between the solid and fluid phases.

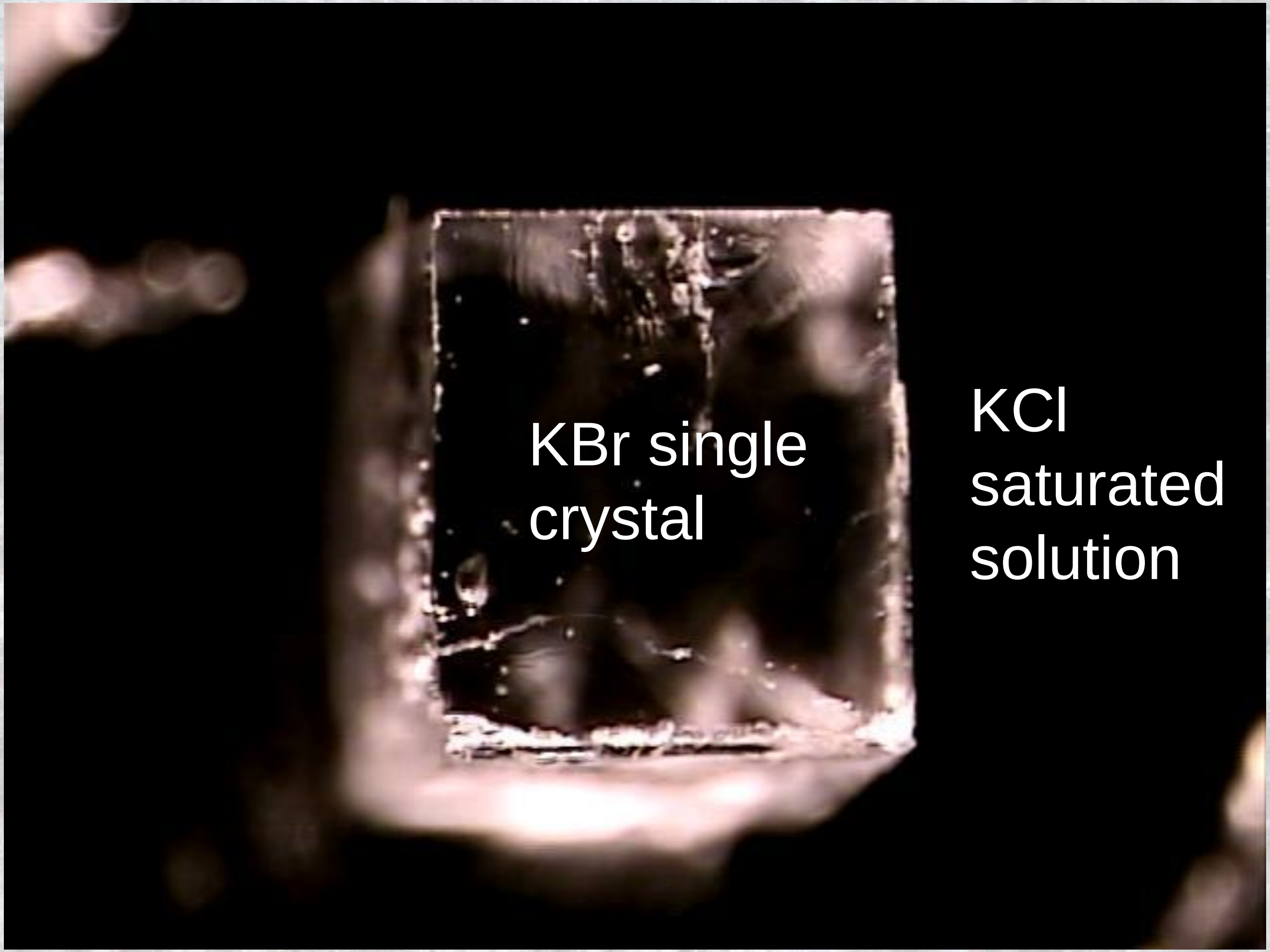
Putnis A. & Putnis C.V. (2007) Journ. Solid State Chemistry 180, 1783
Pollok, Putnis & Putnis *Am.J.Sci*. **311**, 211 (2011)

Example 1:

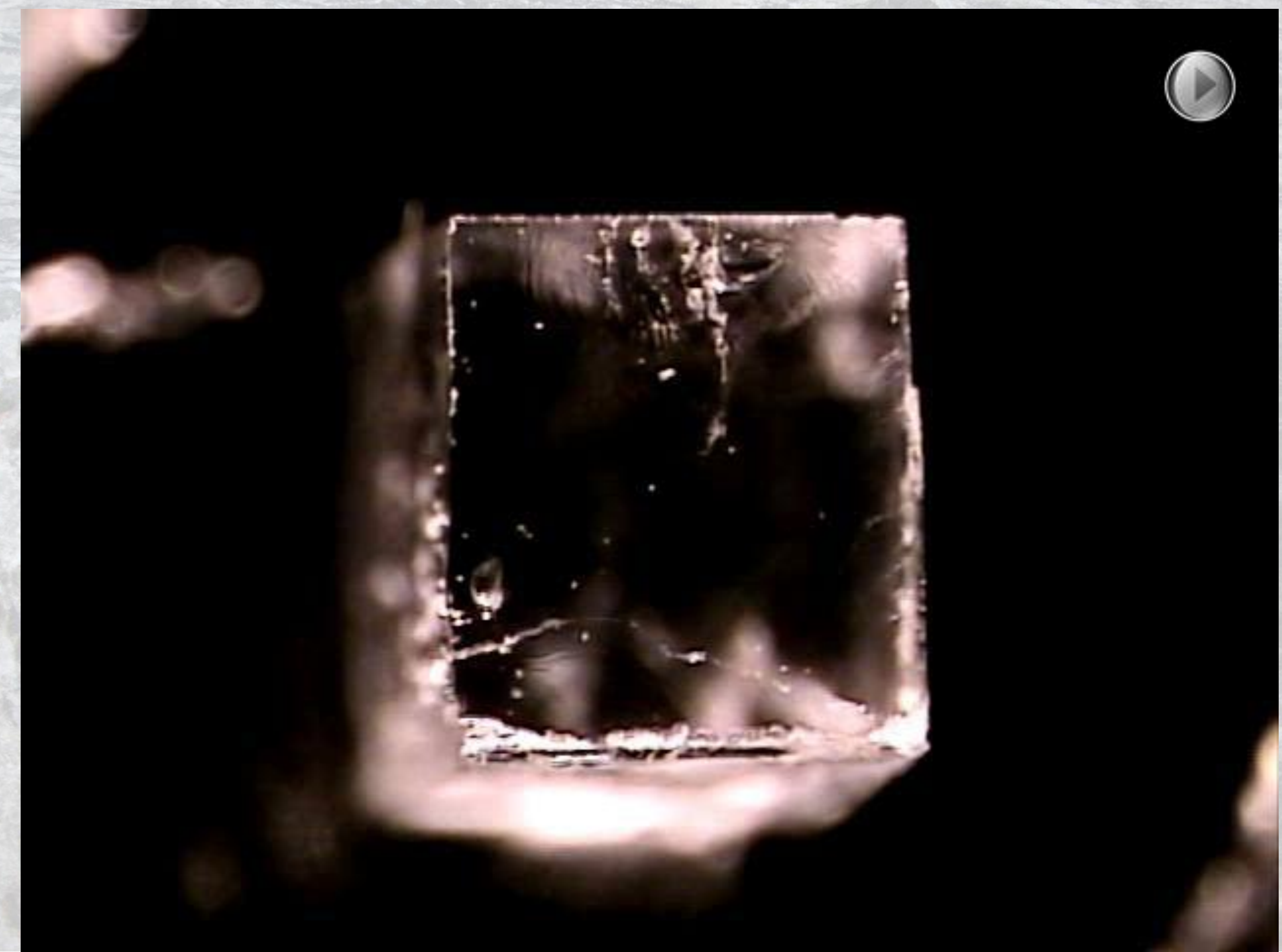
Experiment

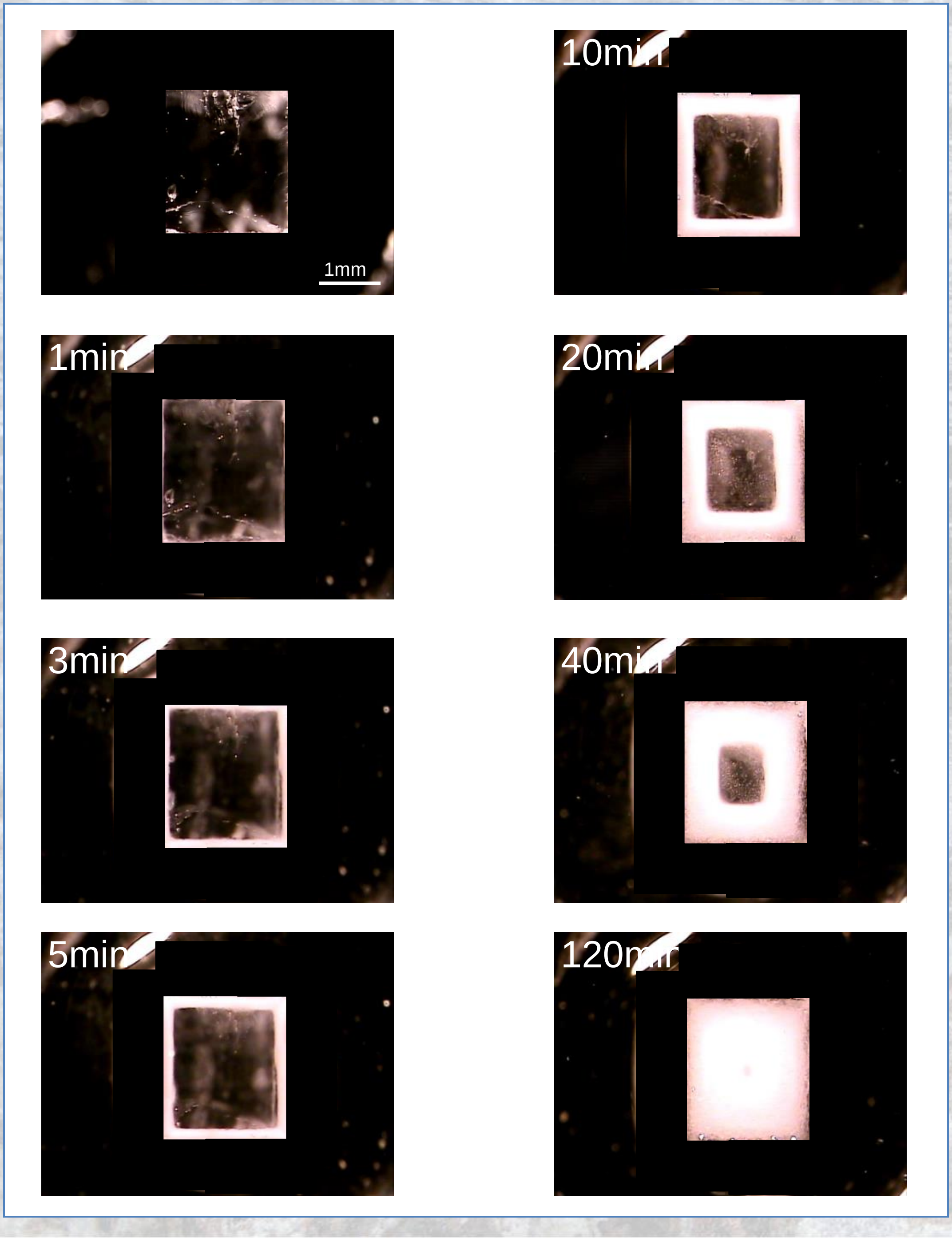
Single crystal of KBr replaced by porous single crystal of KCl

When a single crystal of KBr is immersed in a saturated KCl solution, it is pseudomorphically replaced by a highly porous single crystal of KCl.



When a single crystal of KBr is immersed in a saturated KCl solution, it is pseudomorphically replaced by a highly porous single crystal of KCl.

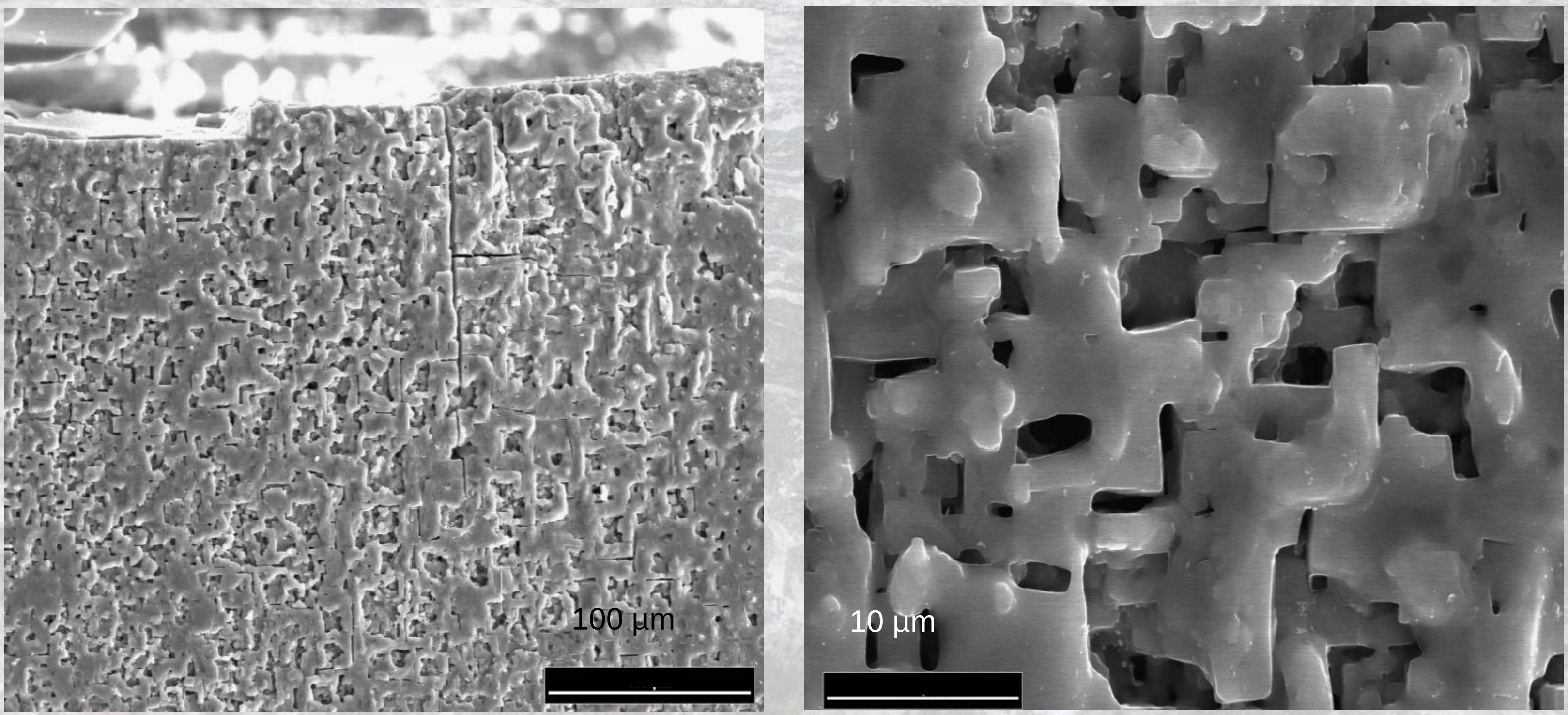




KBr is progressively replaced by a new K(Br,Cl) phase formed at a sharp interface which moves through the crystal.

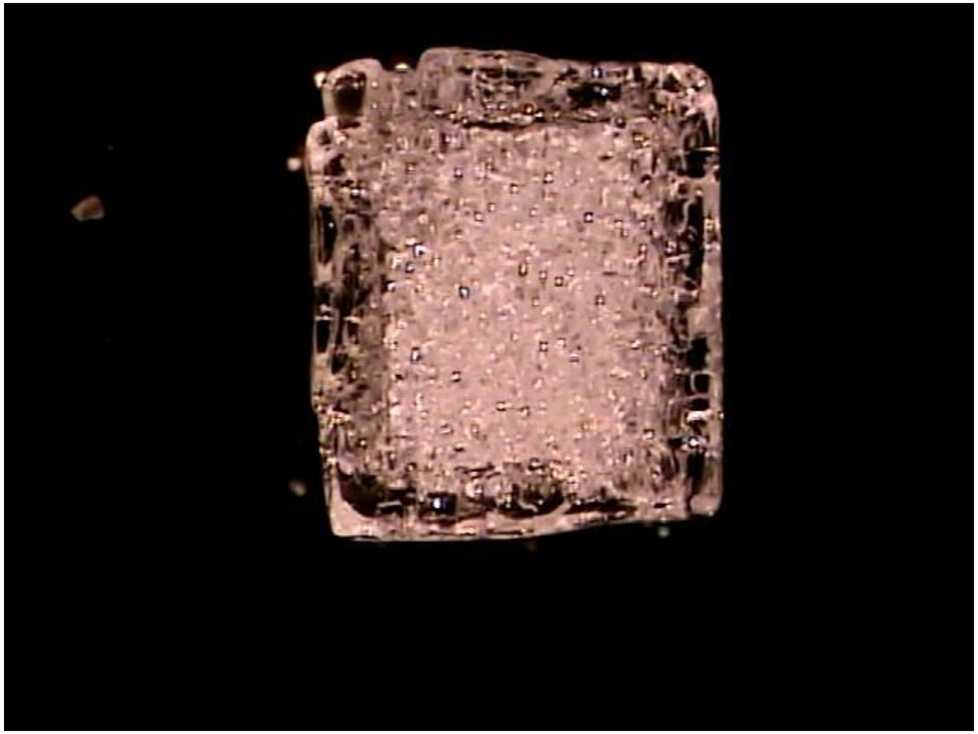
After 2 hours KBr is completely replaced by KCl

The replacement of KBr by KCl - porosity development

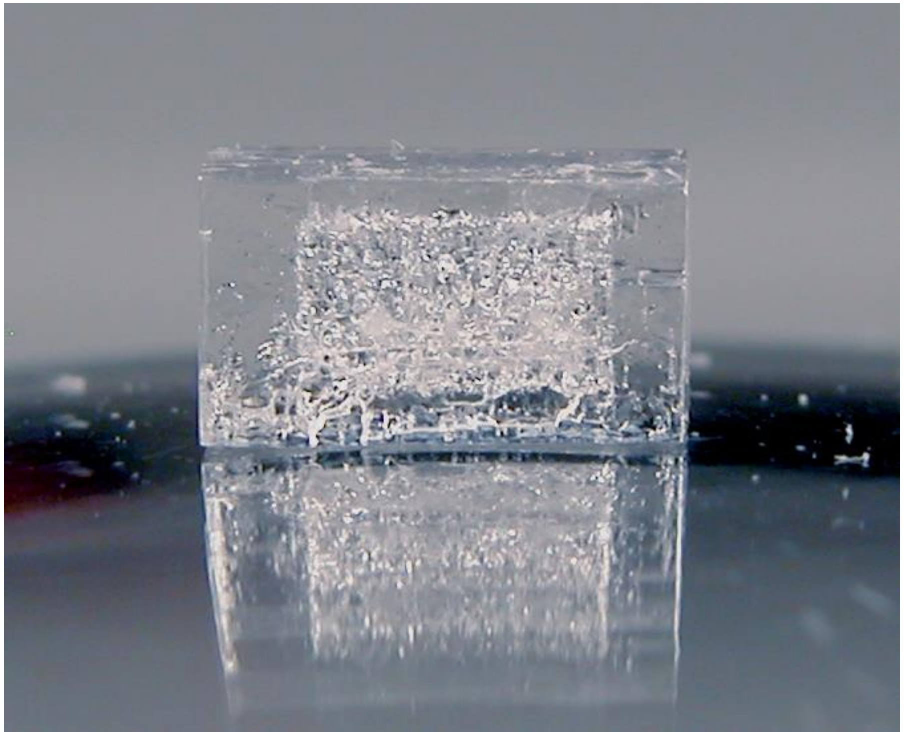


A single crystal of KBr can be replaced by a single crystal of KCl at room temperature (Putnis C.V. et al., 2005)

Porosity coarsening and elimination as a function of time



12 days

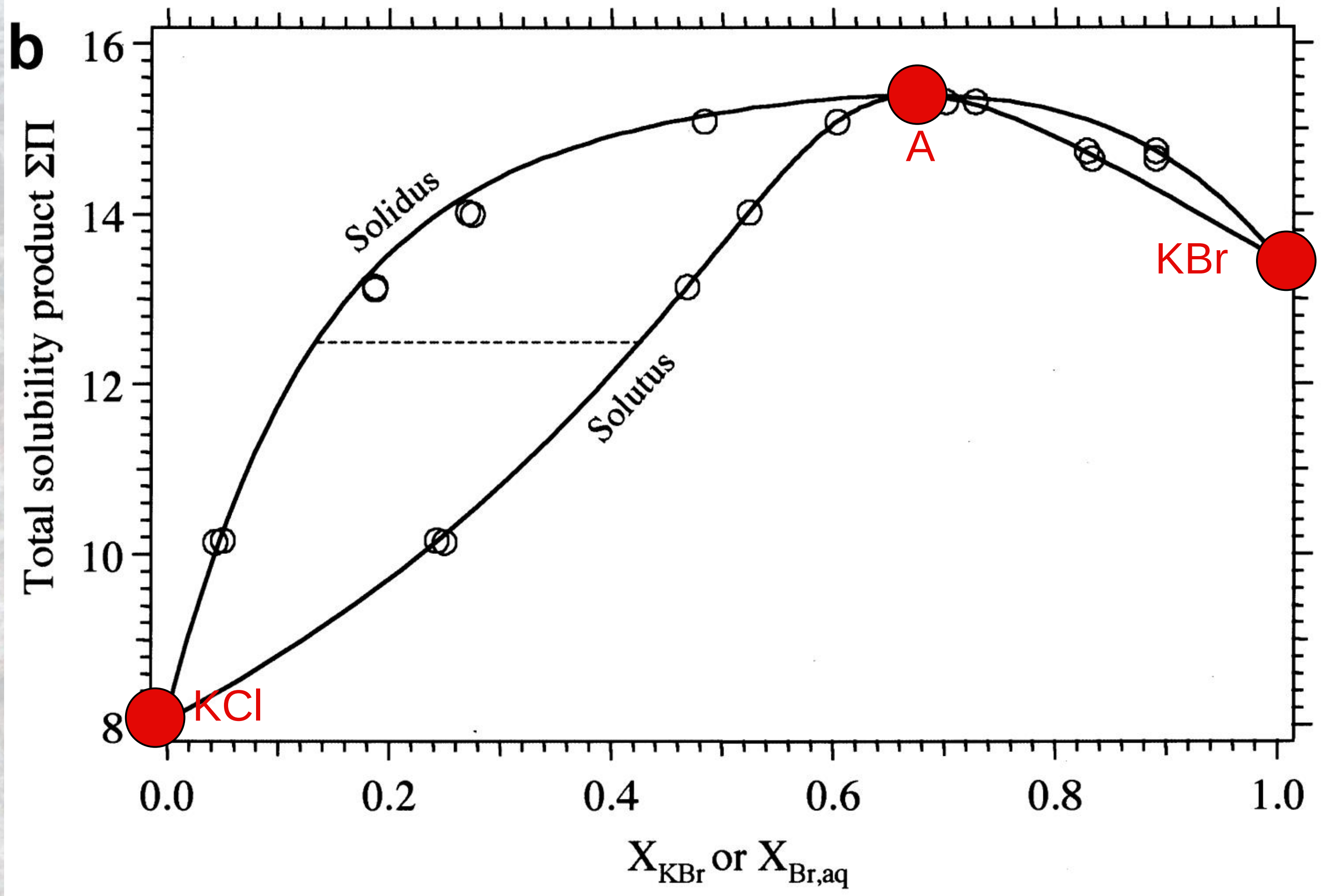


7 weeks

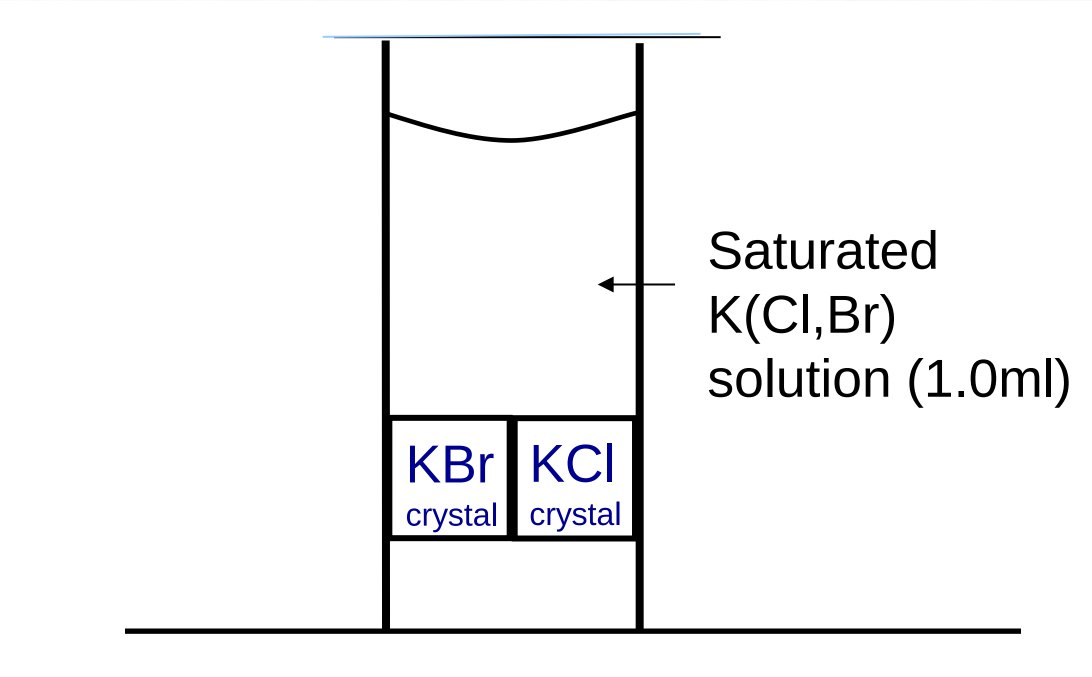
Porosity, like all microstructures, is a transient phenomenon associated with the mechanism and kinetics.

Grain-scale disequilibrium during replacement processes

What will happen if fluid with composition A reacts with an assemblage KBr + KCl ?



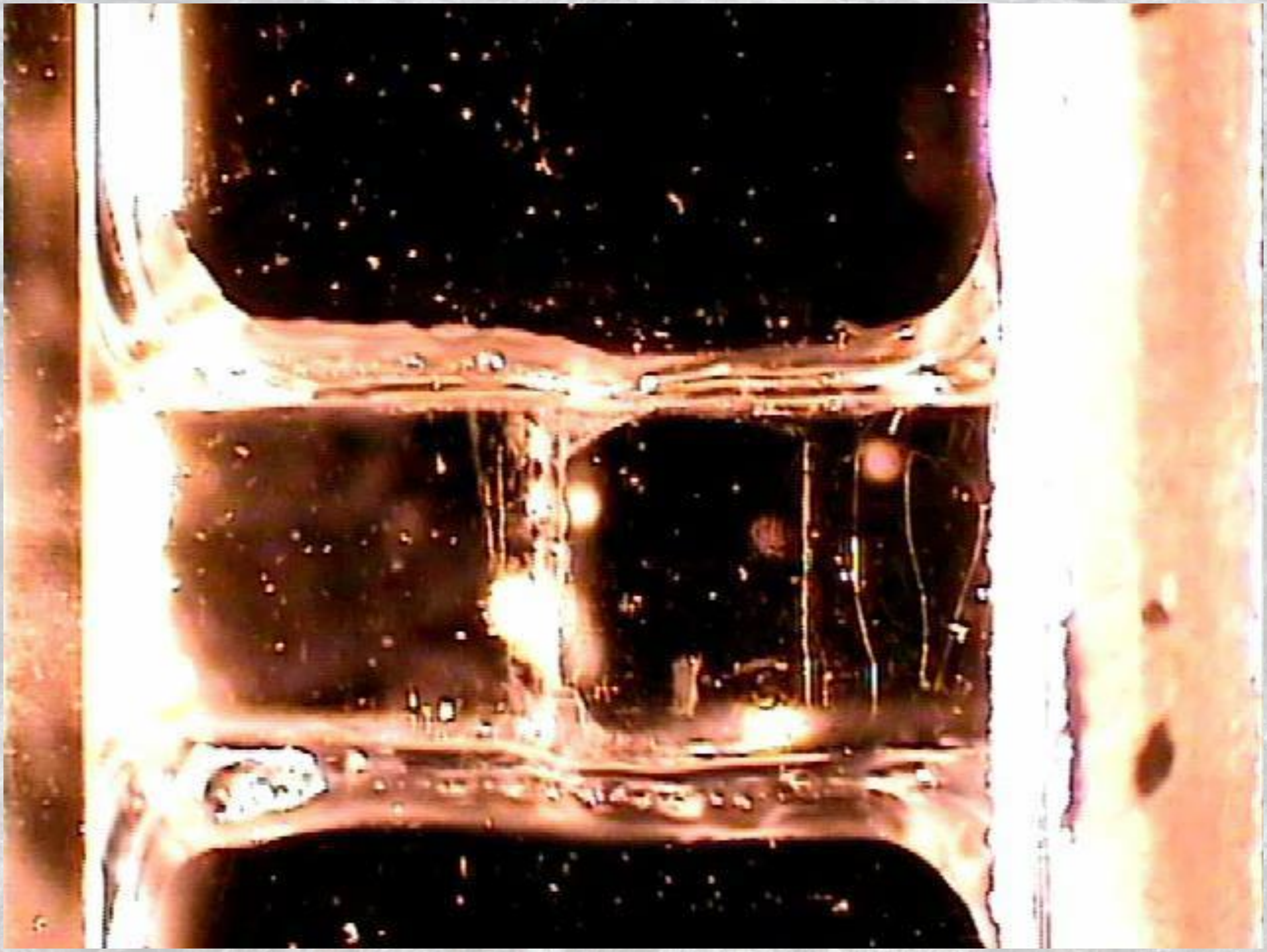
Experimental set up:



2 crystals of KBr and KCl (3 x 5 x 2 mm) were glued with epoxy together and between 4 glass slides to form a container allowing for no grain boundary fluid pathway.

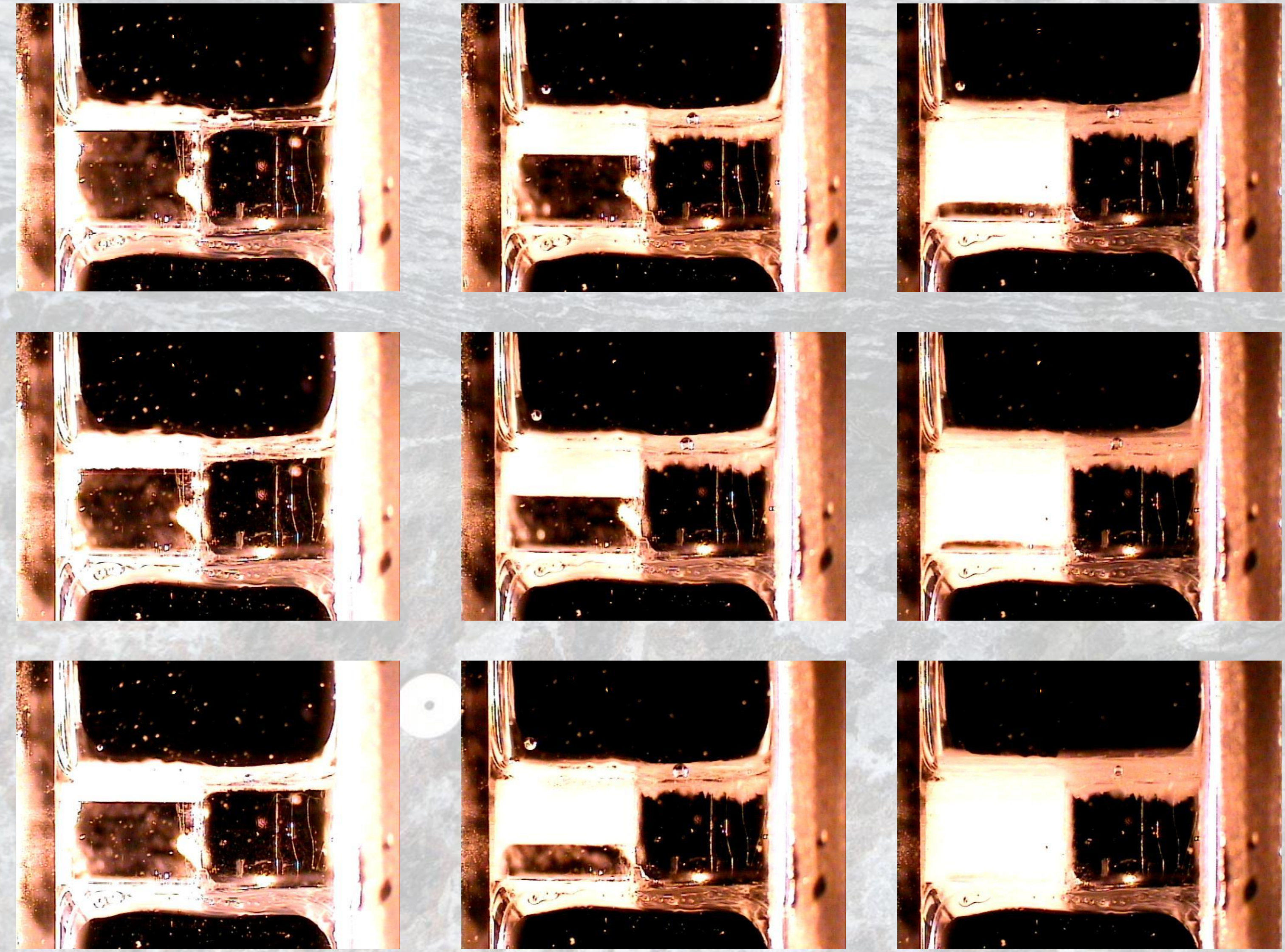
A saturated K(Cl,Br) solution was added above the crystals.

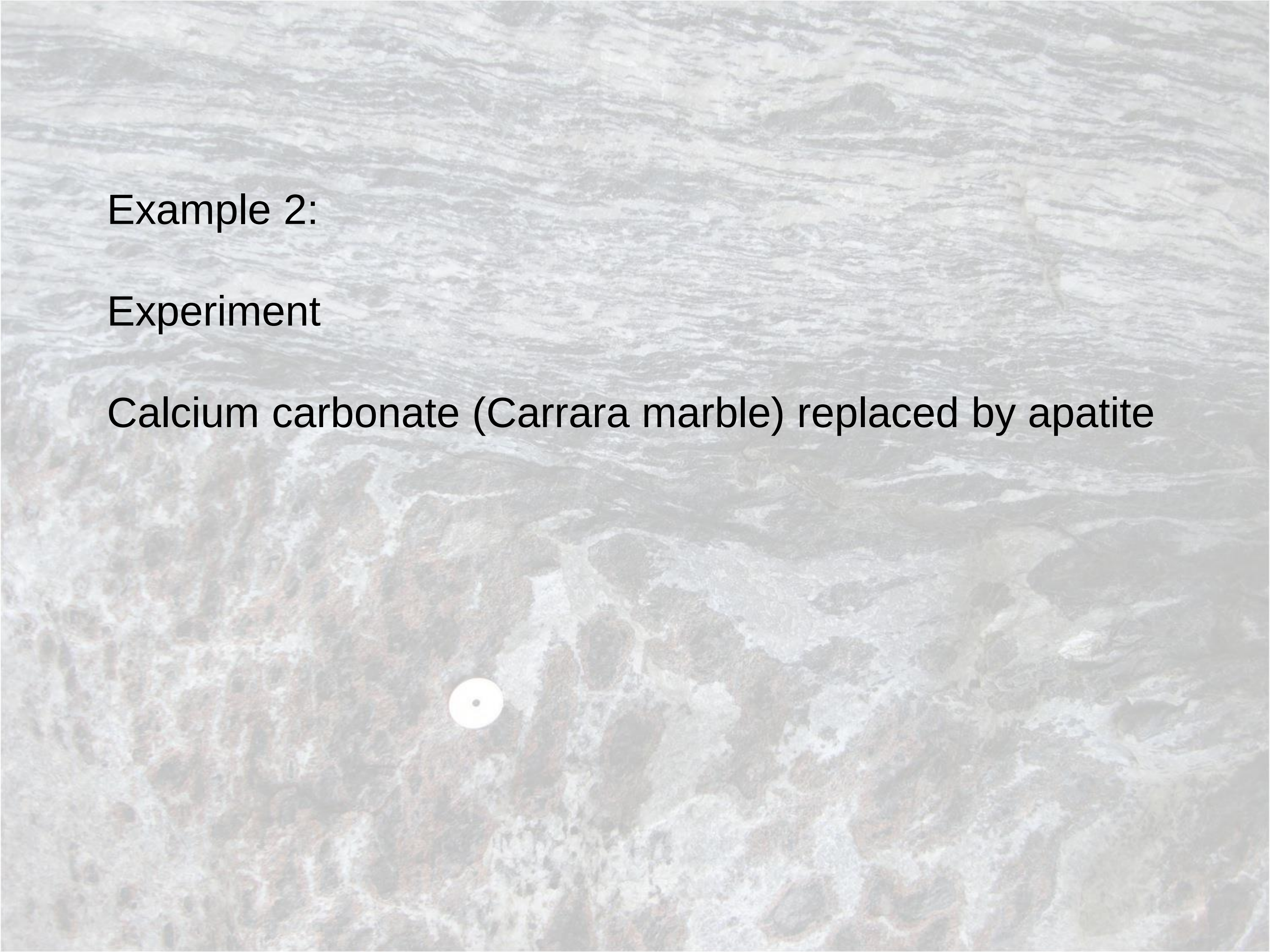
Images were recorded every 5 min using time lapse photography.



Replacement time 125 hours

1mm



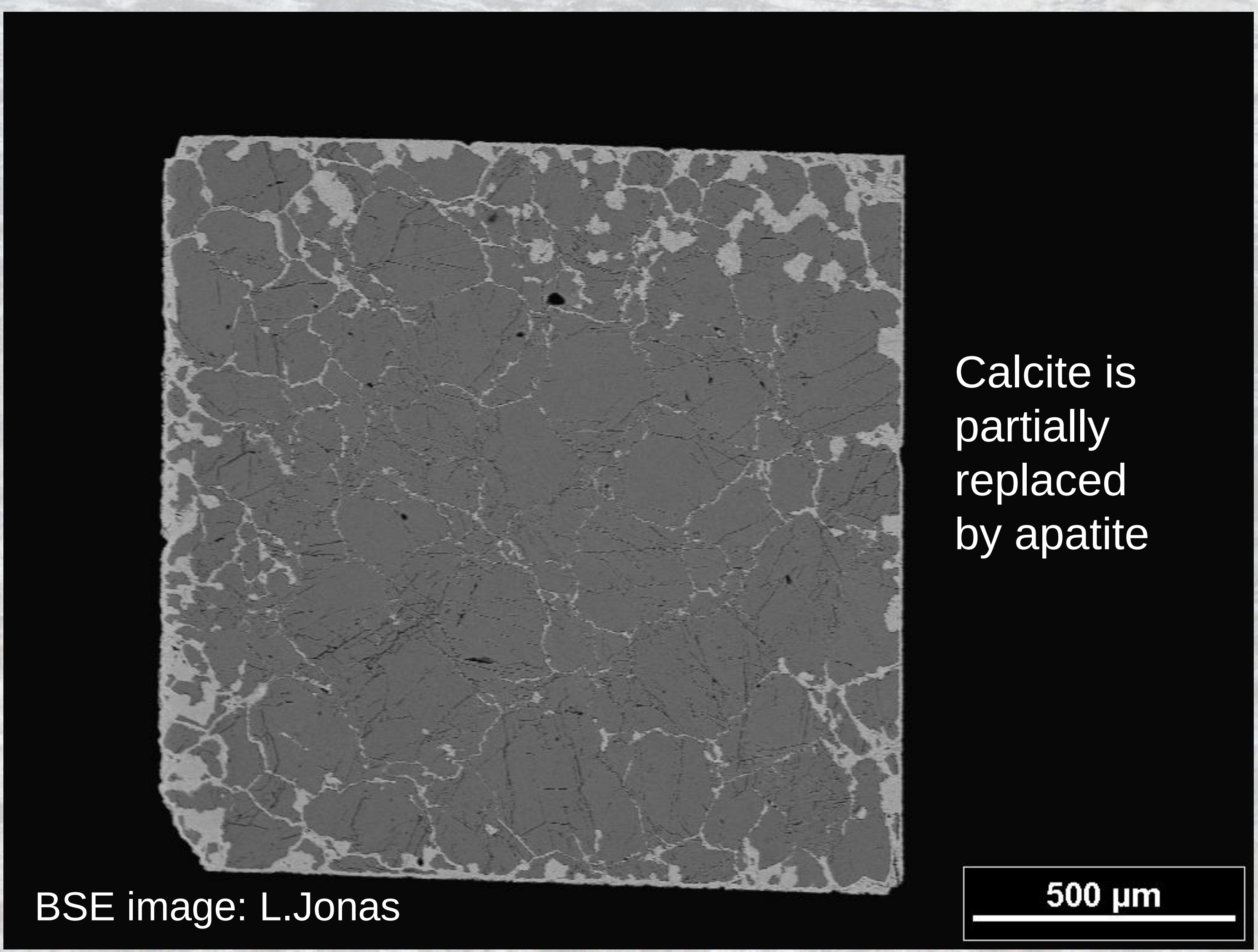


Example 2:

Experiment

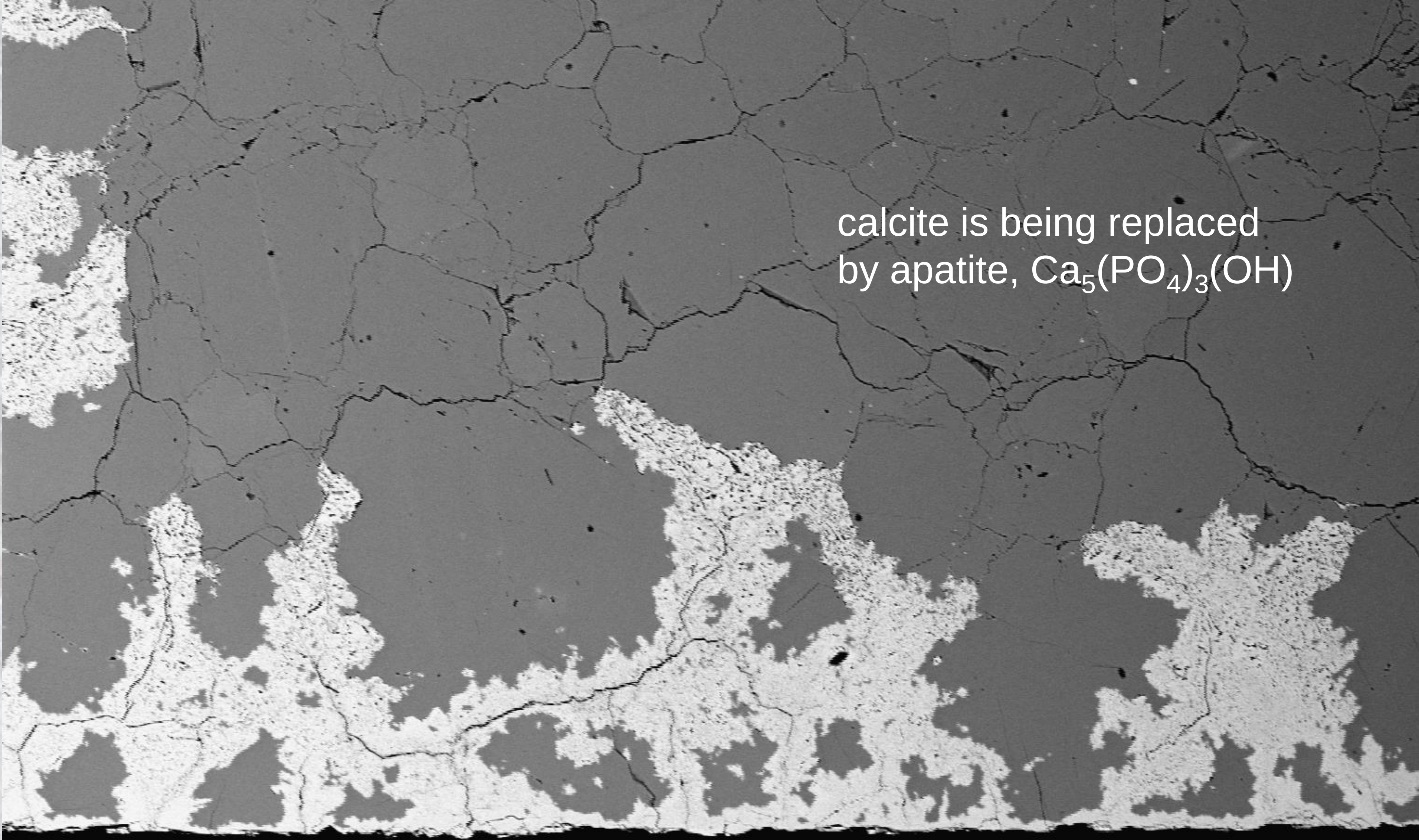
Calcium carbonate (Carrara marble) replaced by apatite

Cross section of cube of Carrara marble reacted with phosphate solution at 150^0C for 1 week



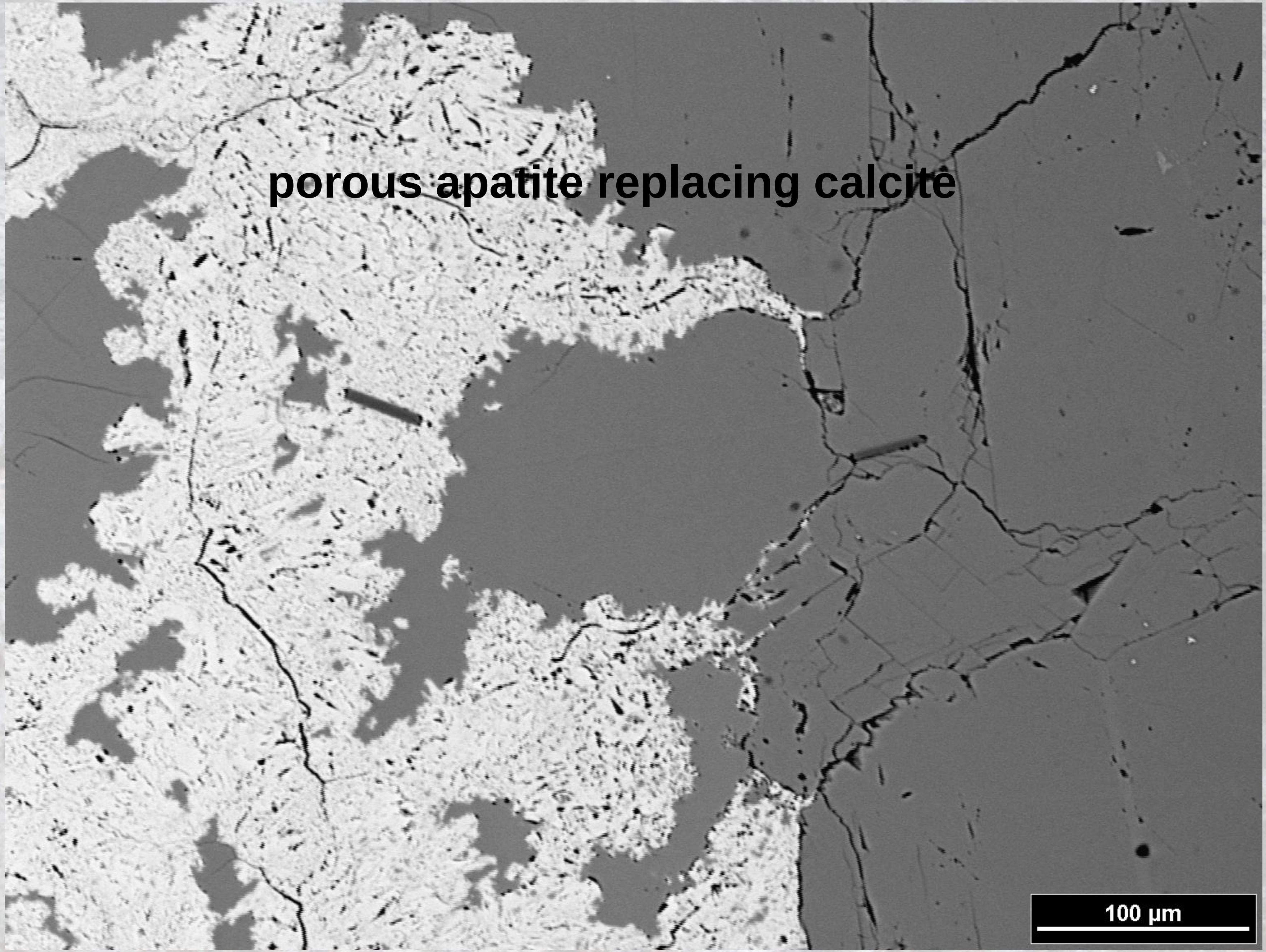
Calcite is partially replaced by apatite

BSE image: L.Jonas



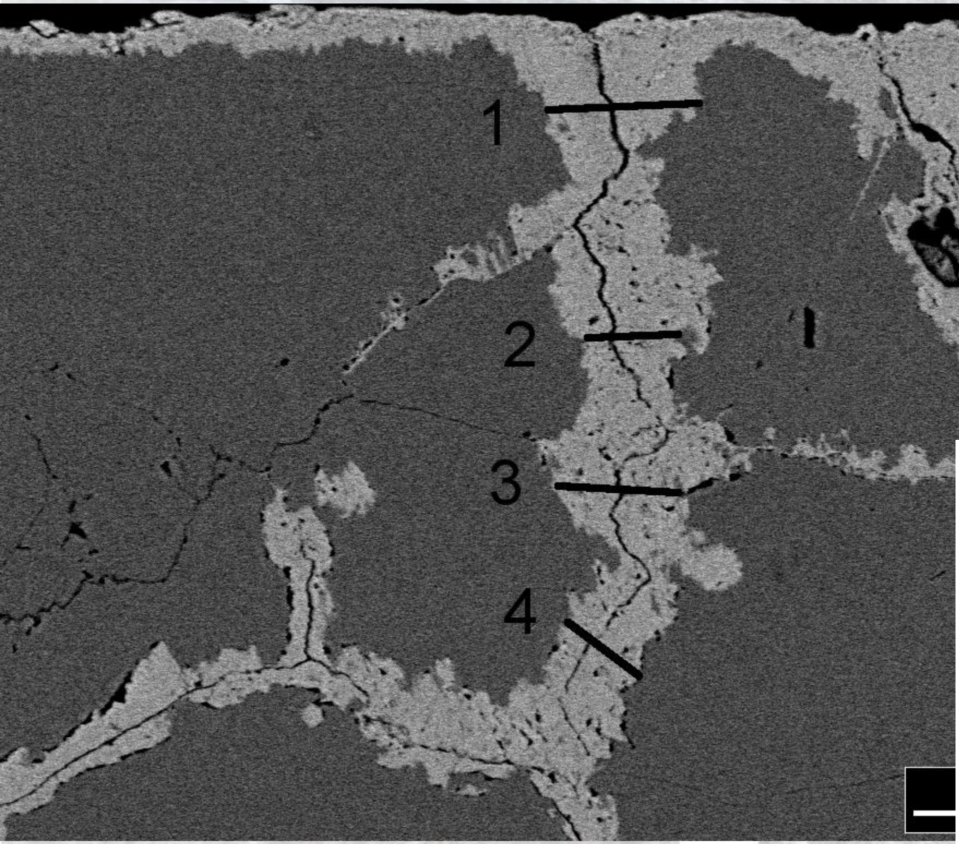
calcite is being replaced by apatite, $Ca_5(PO_4)_3(OH)$

Experiments with Carrara marble with a hydrothermal fluid containing phosphate ions. The dissolution of the calcite results in a Ca-P bearing fluid, from which apatite nucleates. The dissolution and precipitation are coupled so that the parent phase is replaced by the product.

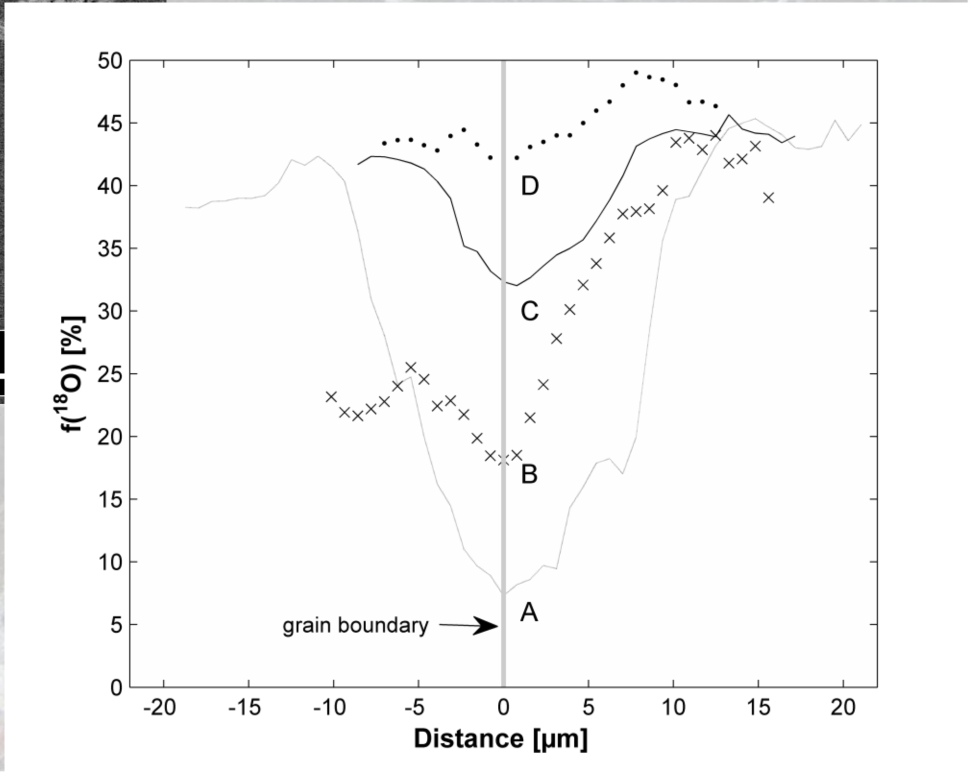


porous apatite replacing calcite

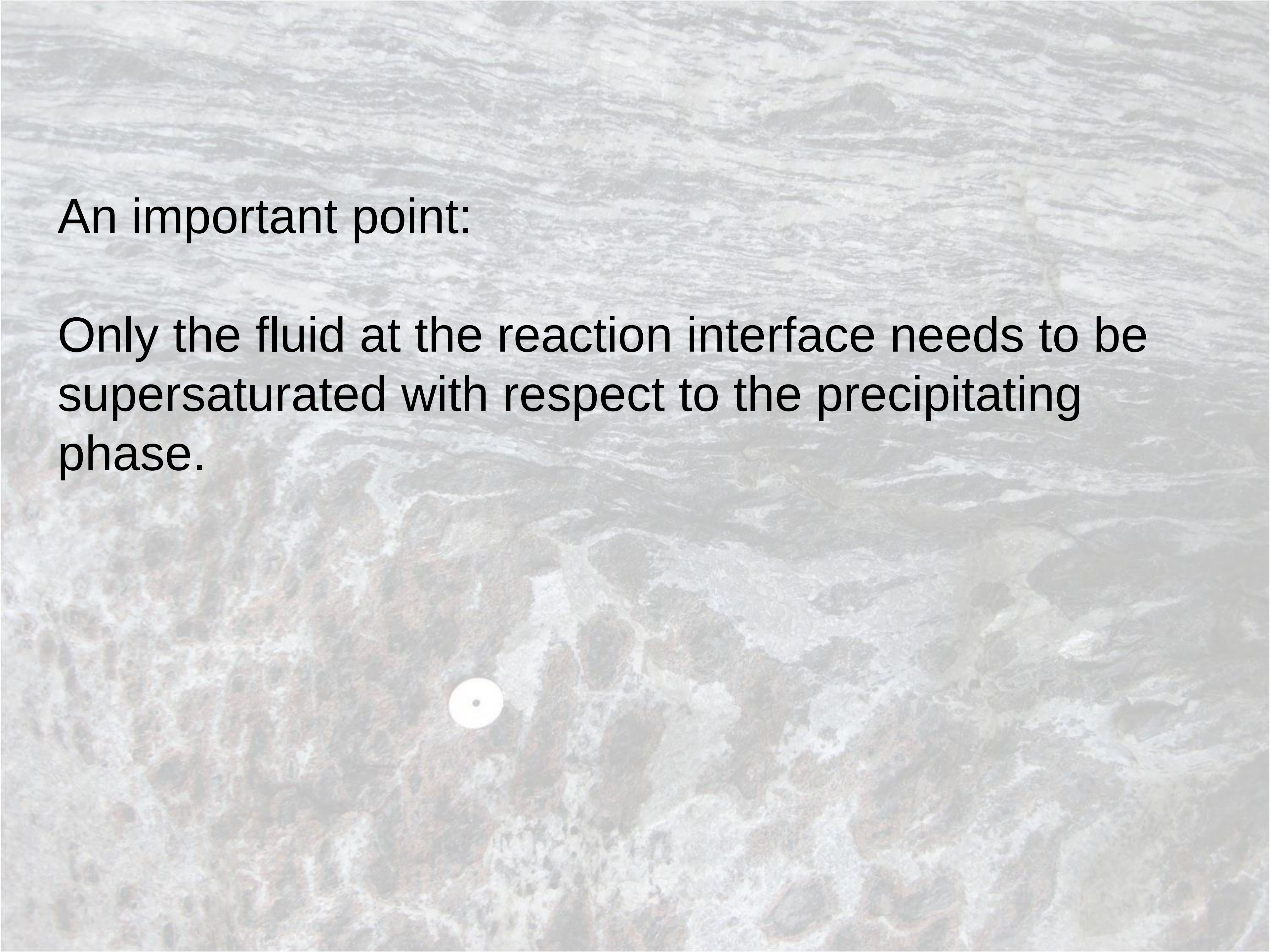
Measuring the ^{18}O content of the apatite as an internal chronometer for the time of replacement at different points.



This depends on the kinetics of the exchange:
$H_2{}^{18}O + P^{16}O_4 = H_2{}^{16}O + P^{18}O_4$
in the solution.

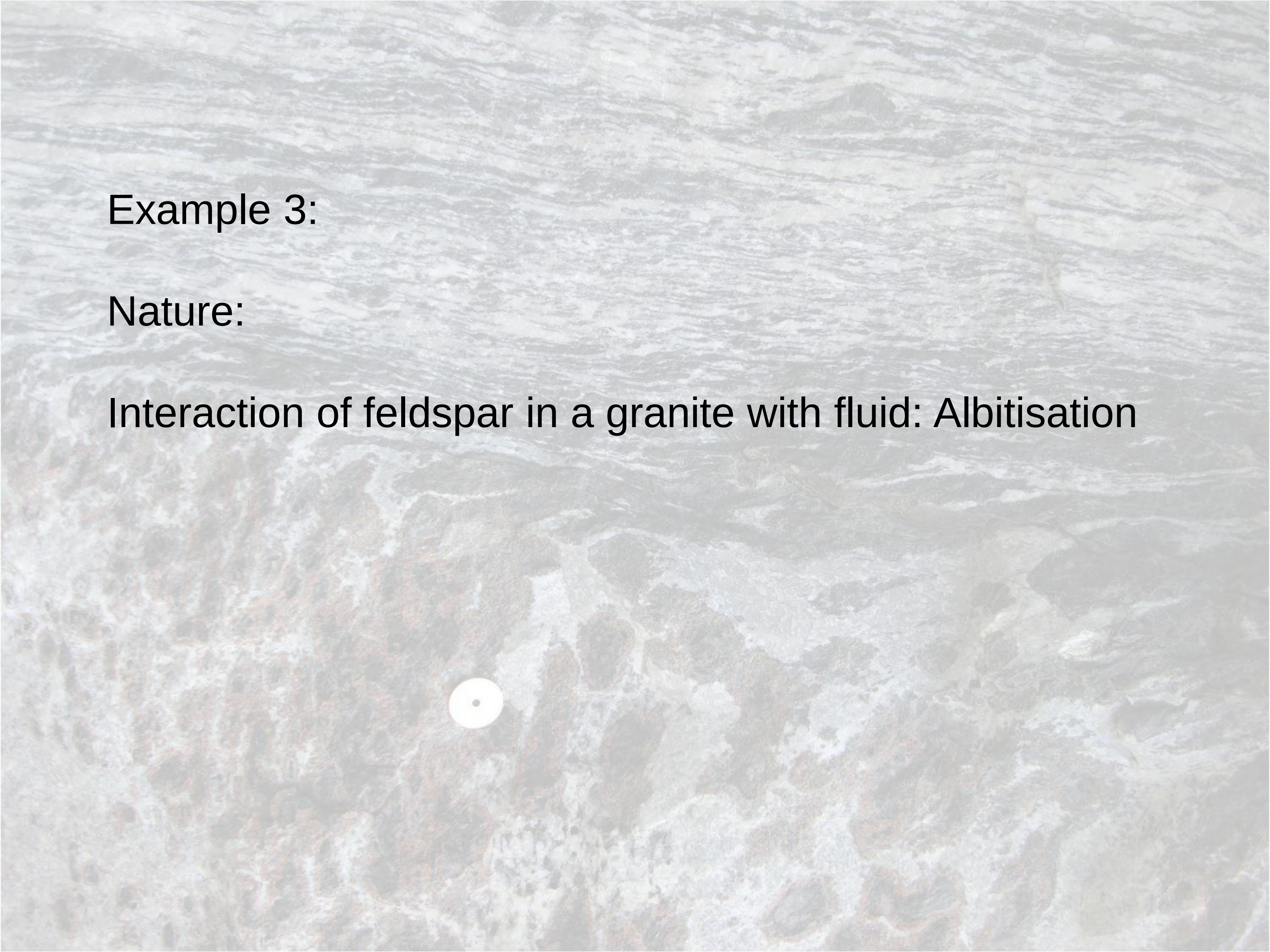


Jonas et al., EPSL In review



An important point:

Only the fluid at the reaction interface needs to be supersaturated with respect to the precipitating phase.



Example 3:

Nature:

Interaction of feldspar in a granite with fluid: Albitisation

Albitisation in the Bamble Sector, south eastern Norway

Albitisation may also be associated with hematite precipitation

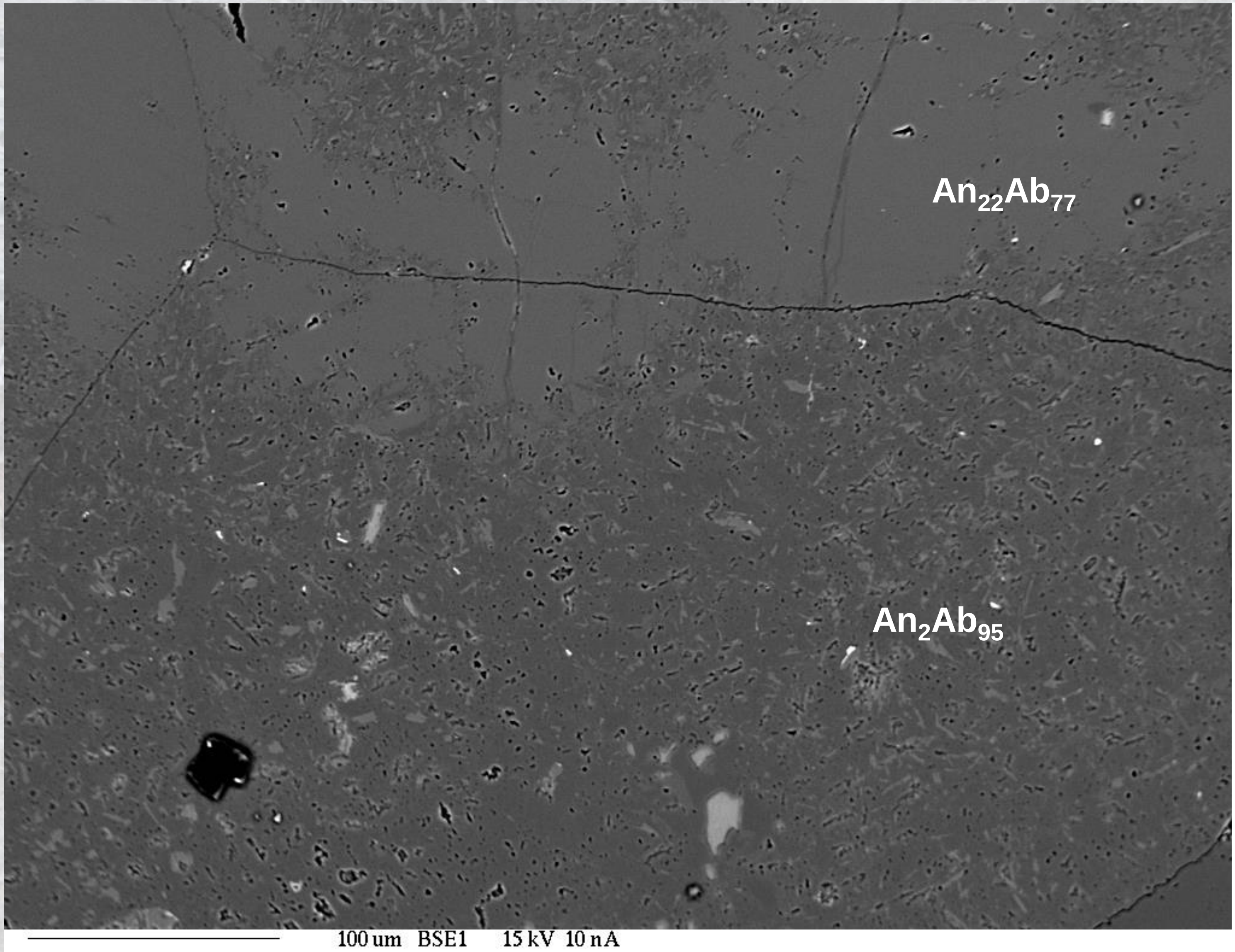
EXAMPLE:

Fluid - induced chemical reequilibration of feldspars

Albitisation of granitoid in the Bamble sector, Norway

Plagioclase (Na,Ca) feldspar replaced by albite ($NaAlSi_3O_8$)

Feldspar replacement microstructure



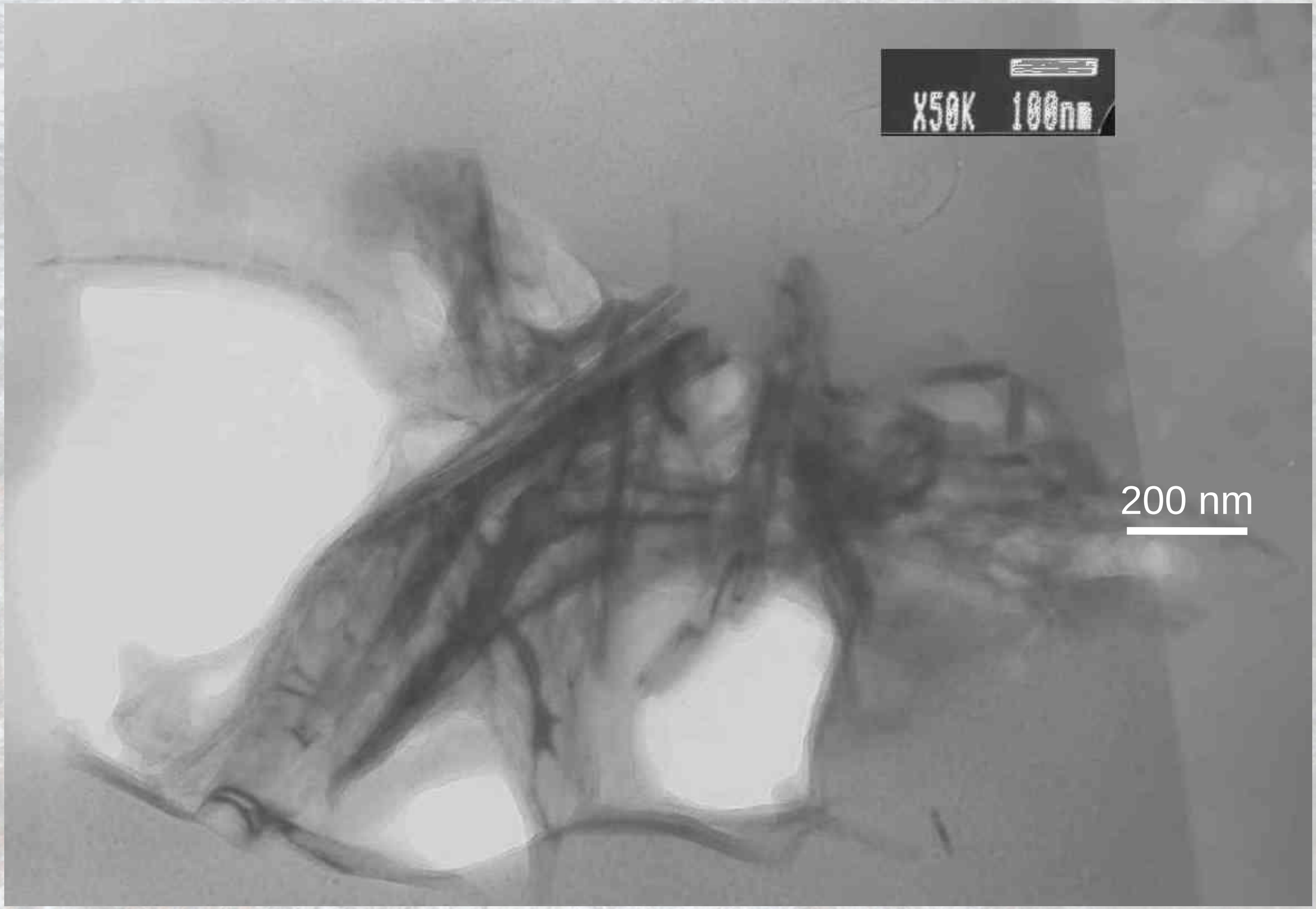
Note the porosity developed in the product phase

The crystal structure is preserved across the sharp interface

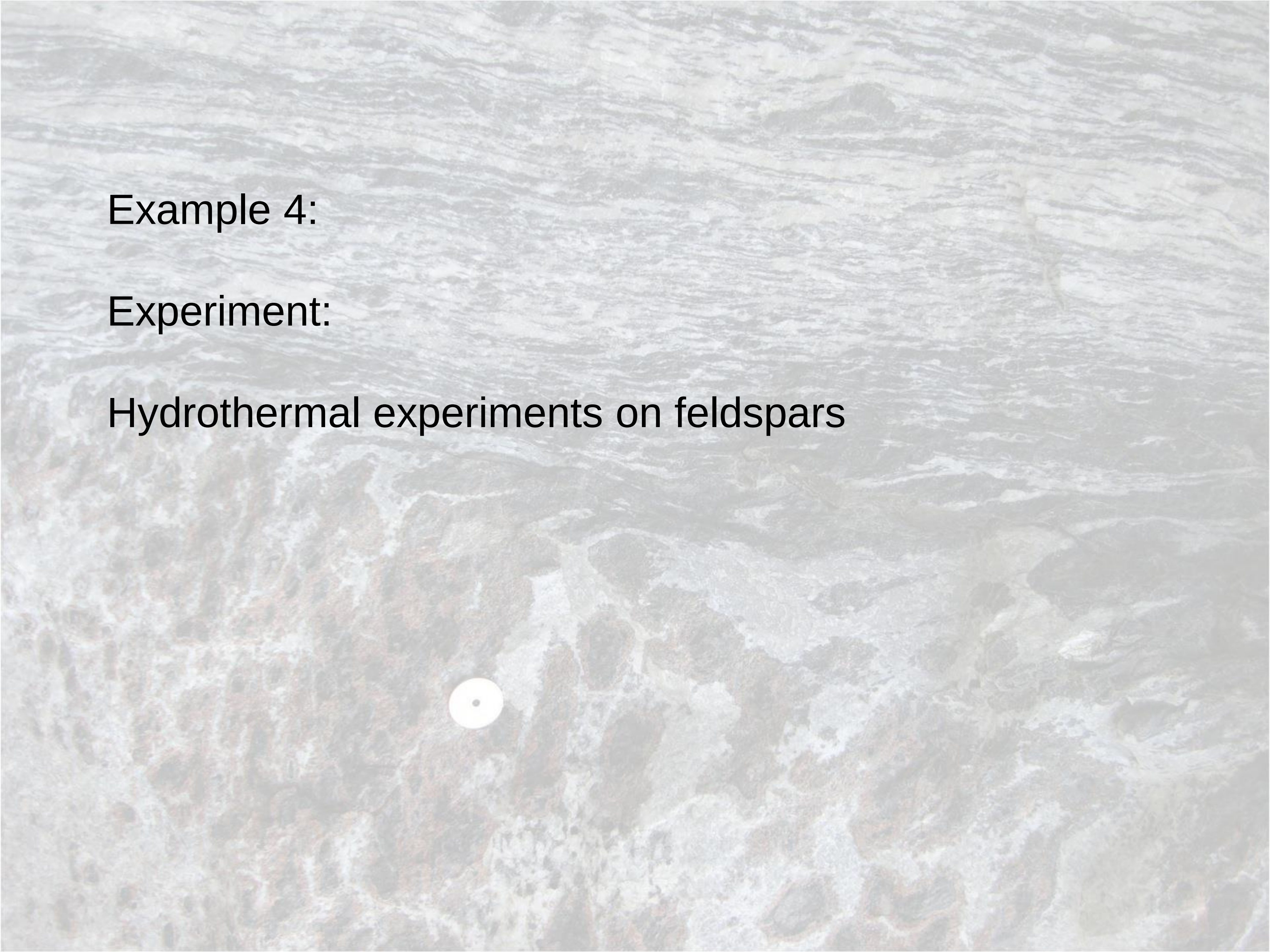
Engvik et al. *Can. Mineral.* **46**, 1401 (2008)

Pink feldspars are the result of replacement

Nano-pores in the pink feldspar are filled with hematite, precipitated from the fluid during the replacement



Putnis et al., *Lithos*, **95**, 10 (2007)



Example 4:

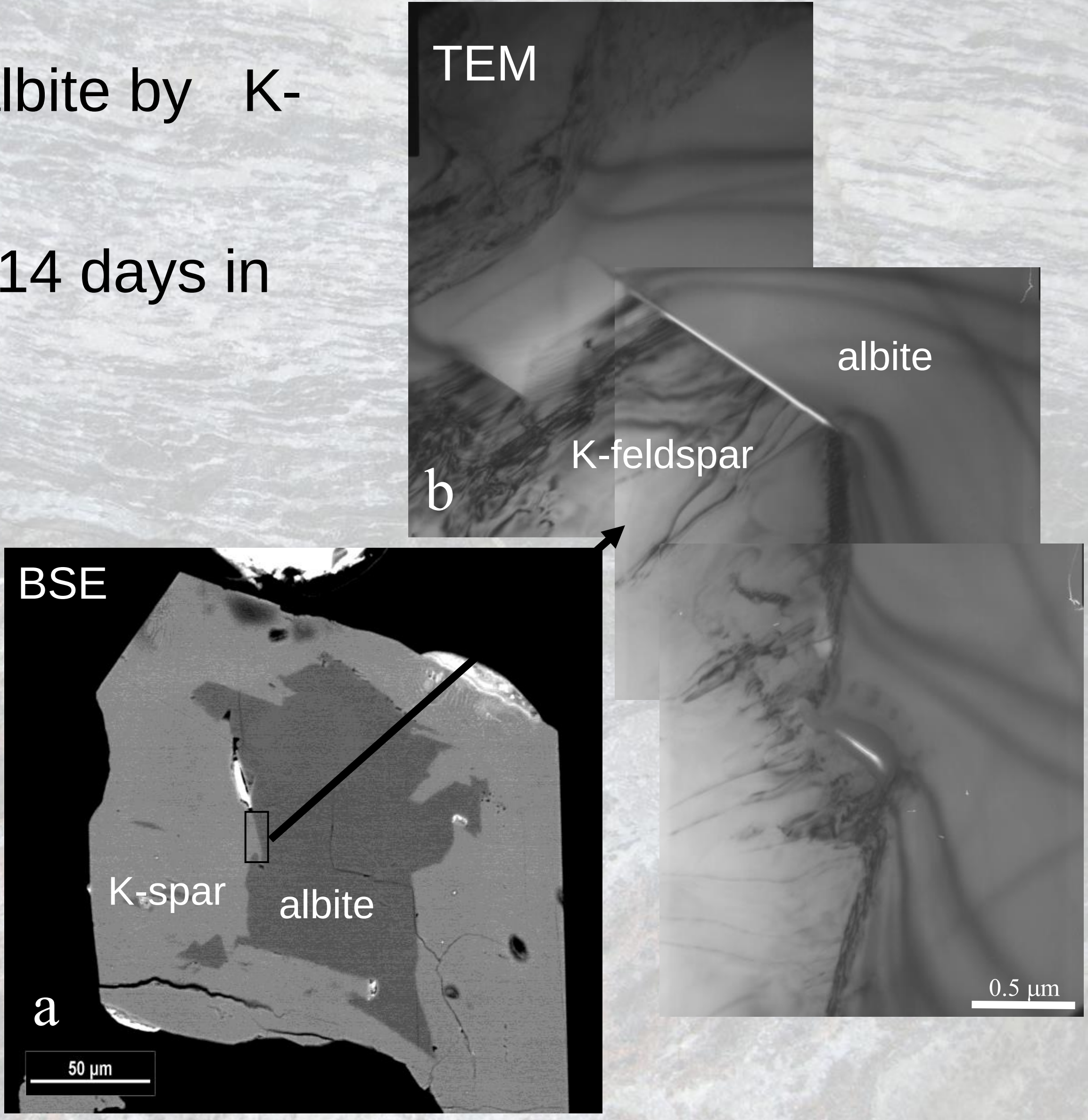
Experiment:

Hydrothermal experiments on feldspars

Experiment:

Replacement of albite by K-feldspar

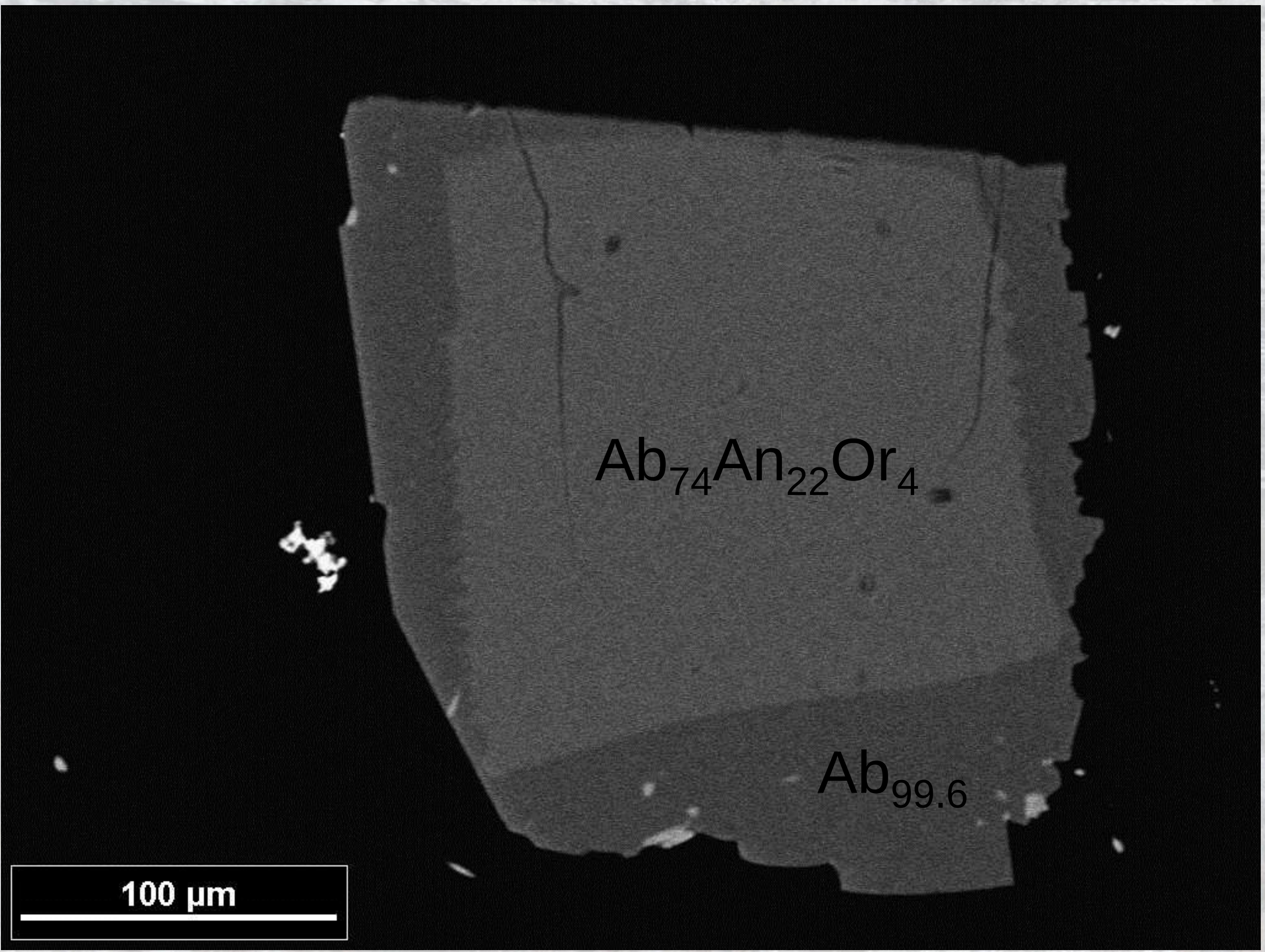
600^{0}C 2kbars 3-14 days in KCl soln.



The porosity in the K-feldspar product is on a nano-scale

Niedermeier et al., *Contribs. Min. Pet.* **157**, 65 (2009)

Experimental albitisation



Starting with Oligoclase An_{22}

In aqueous solution containing Na and Si

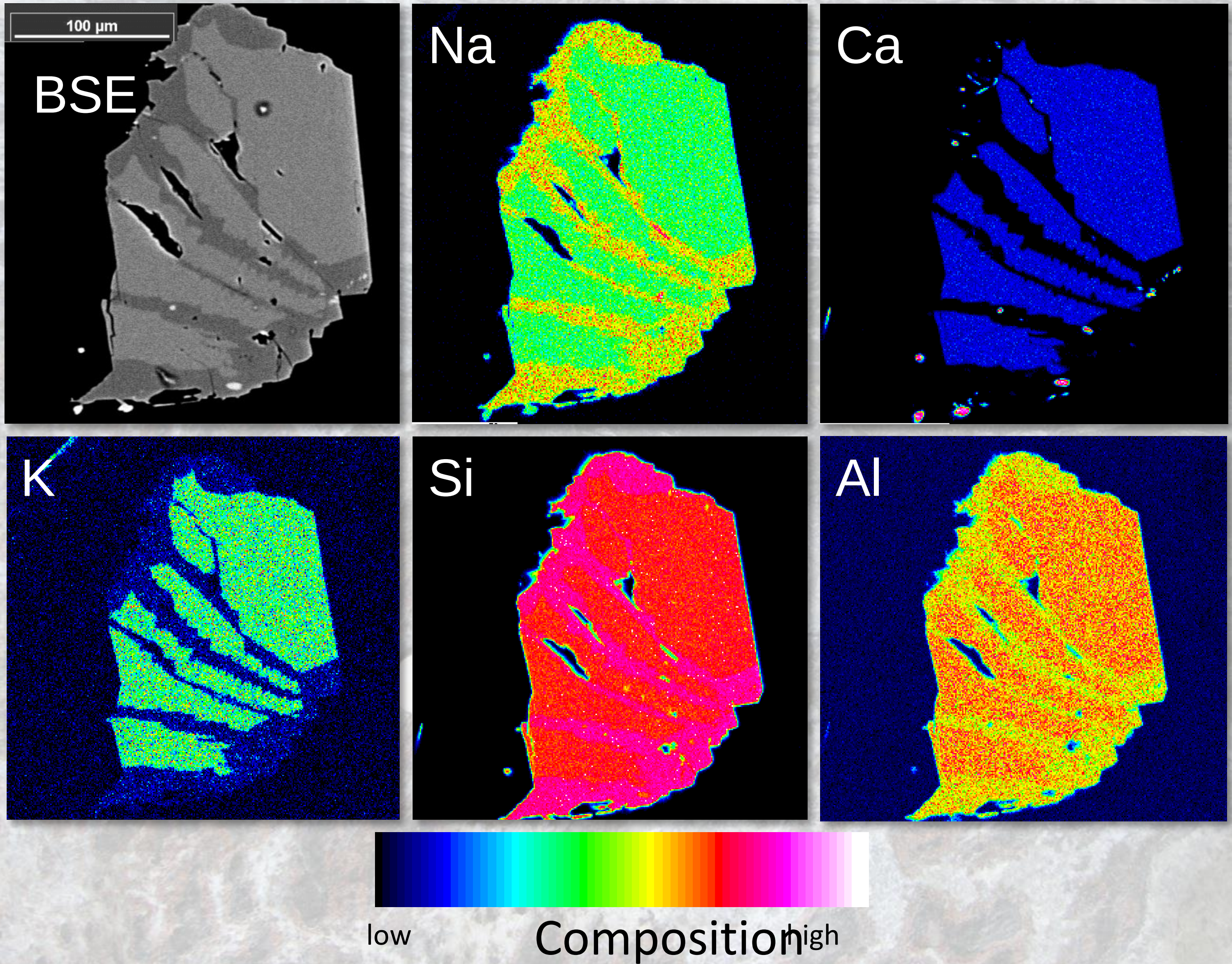
$T=600^oC$

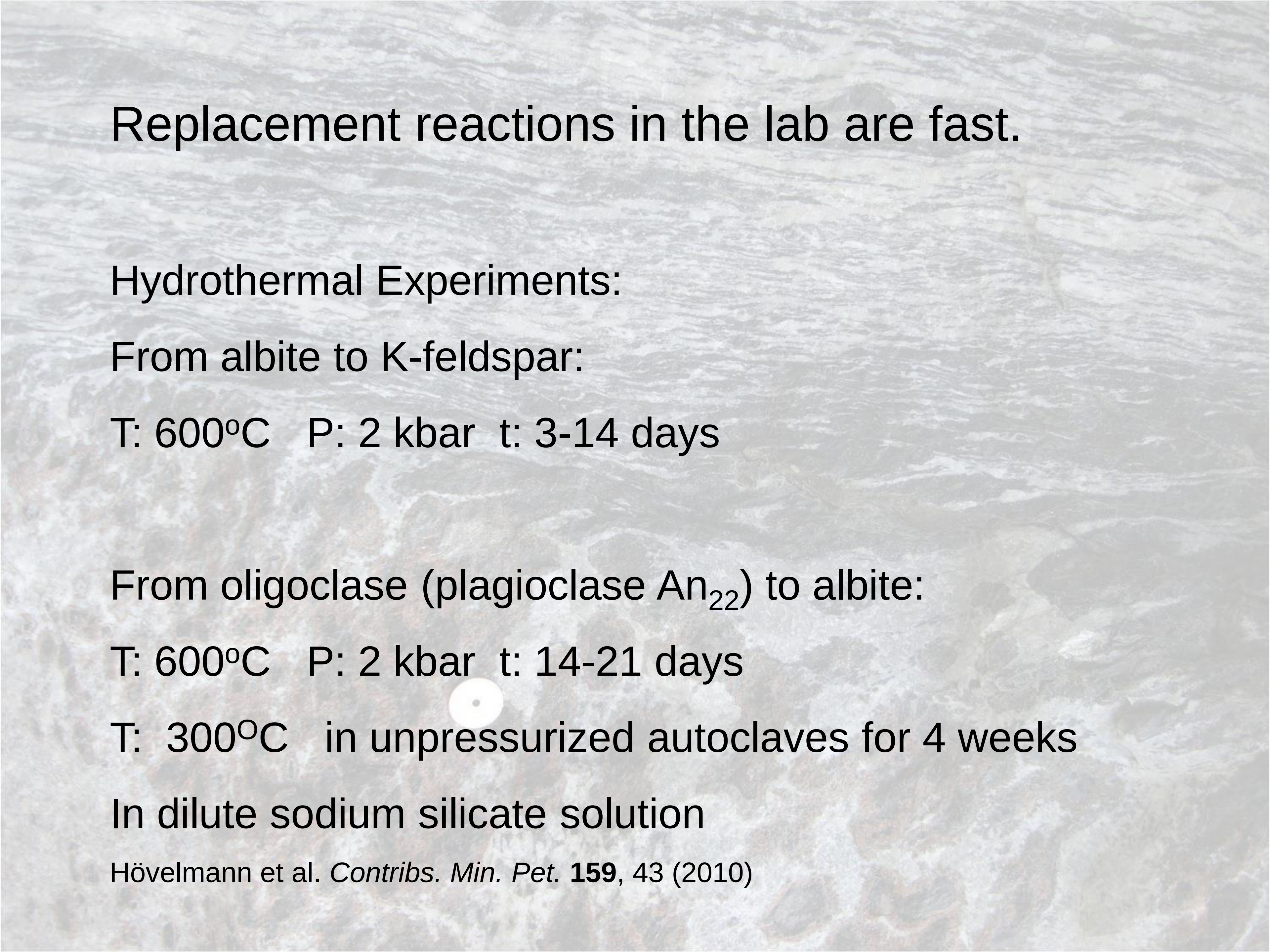
$P = 2$ kbar

$t = 17$ days

Hövelmann et al. *Contribs. Min. Pet.* **159**, 43 (2010)

Experimental albitisation Element maps





Replacement reactions in the lab are fast.

Hydrothermal Experiments:

From albite to K-feldspar:

T: 600^{o}C   P: 2 kbar t: 3-14 days

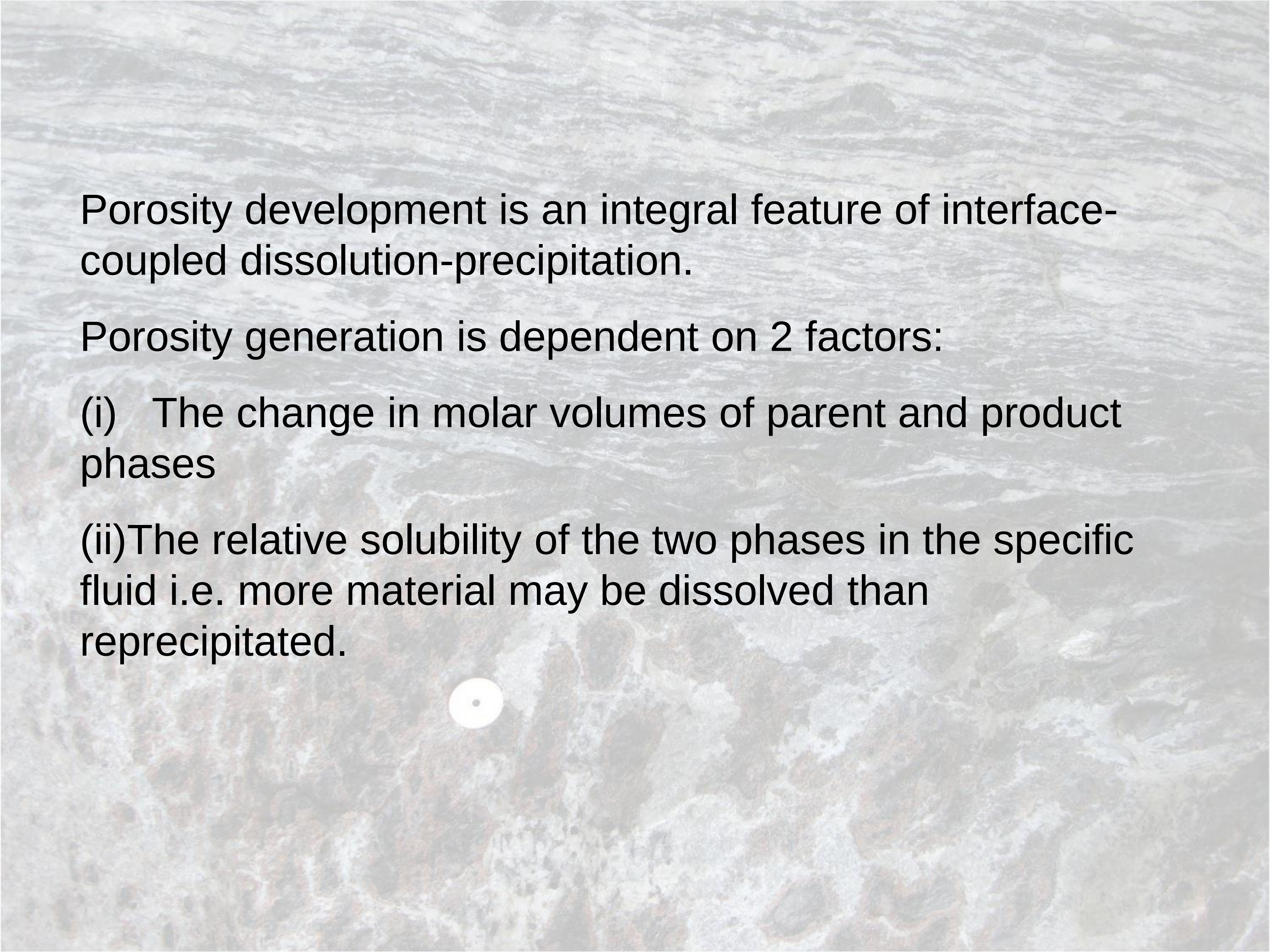
From oligoclase (plagioclase An_{22}) to albite:

T: 600^{o}C   P: 2 kbar t: 14-21 days

T: 300^{O}C   in unpressurized autoclaves for 4 weeks

In dilute sodium silicate solution

Hövelmann et al. *Contribs. Min. Pet.* **159**, 43 (2010)

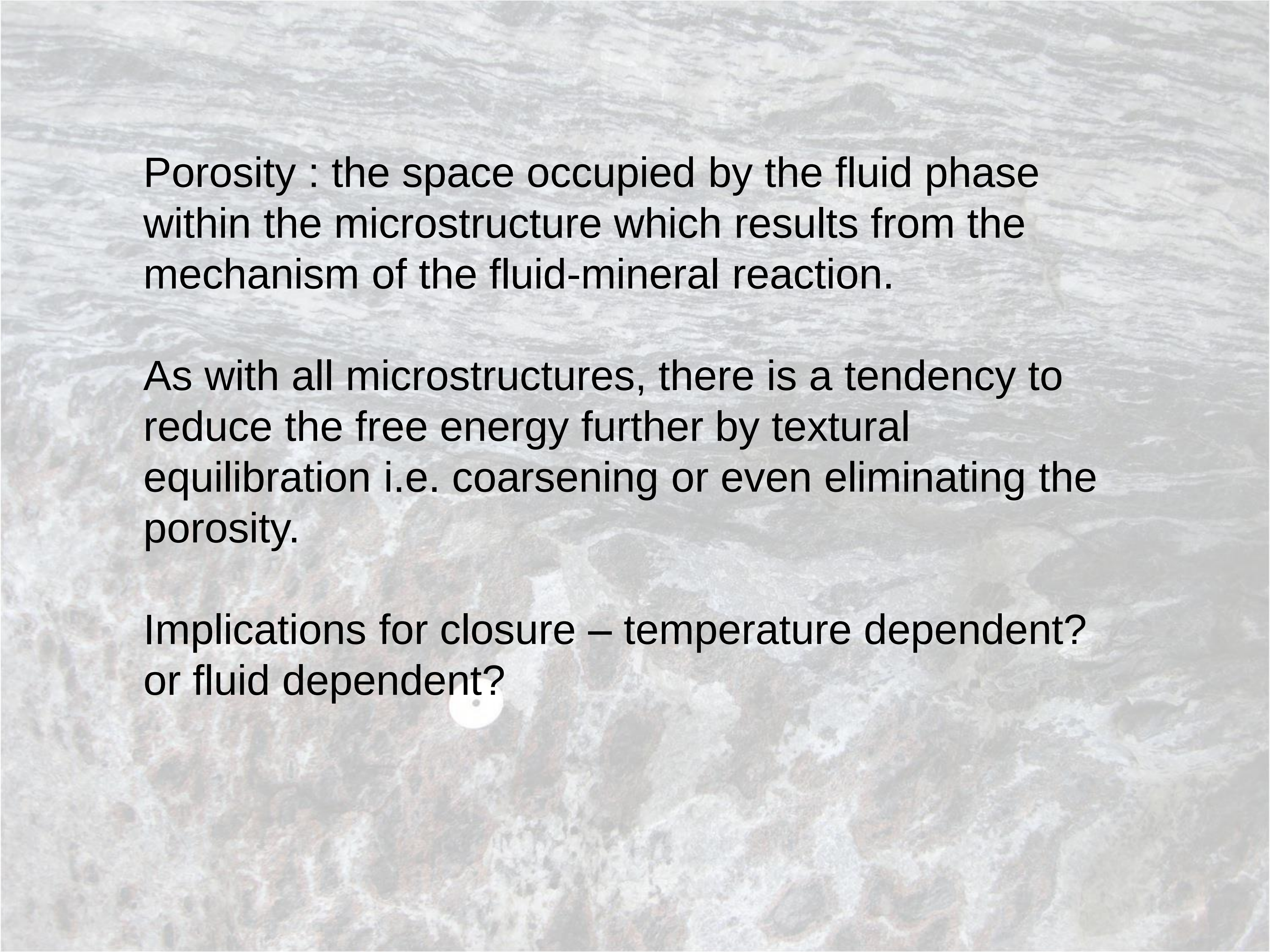


Porosity development is an integral feature of interface-coupled dissolution-precipitation.

Porosity generation is dependent on 2 factors:

(i) The change in molar volumes of parent and product phases

(ii)The relative solubility of the two phases in the specific fluid i.e. more material may be dissolved than reprecipitated.



Porosity : the space occupied by the fluid phase within the microstructure which results from the mechanism of the fluid-mineral reaction.

As with all microstructures, there is a tendency to reduce the free energy further by textural equilibration i.e. coarsening or even eliminating the porosity.

Implications for closure – temperature dependent? or fluid dependent?

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Journal of Solid State Chemistry 180 (2007) 1783–1786

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Rapid communication

The mechanism of reequilibration of solids in the presence of a fluid phase

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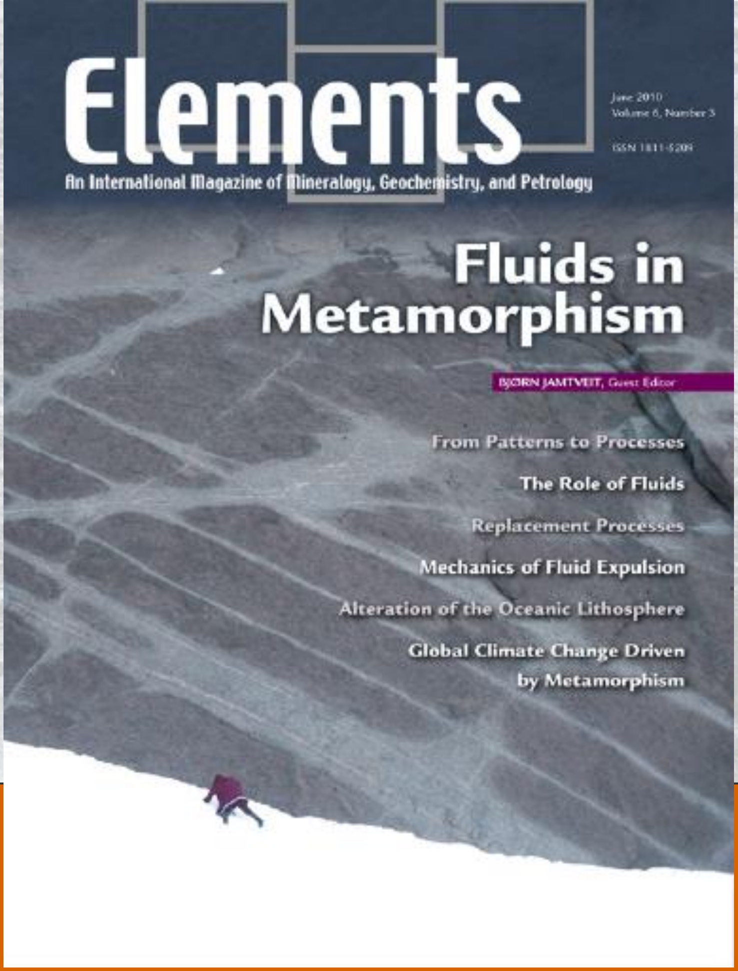
Received 8 March 2007; accepted 24 March 2007
Available online 28 March 2007


Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology

June 2010
Volume 6, Number 3

ISSN 1811-5209

Fluids in Metamorphism

BJØRN JAMTVEIT, Guest Editor

From Patterns to Processes

The Role of Fluids

Replacement Processes

Mechanics of Fluid Expulsion

Alteration of the Oceanic Lithosphere

Global Climate Change Driven by Metamorphism

Replacement Processes in the Earth's Crust

Andrew Putnis* and Timm John*

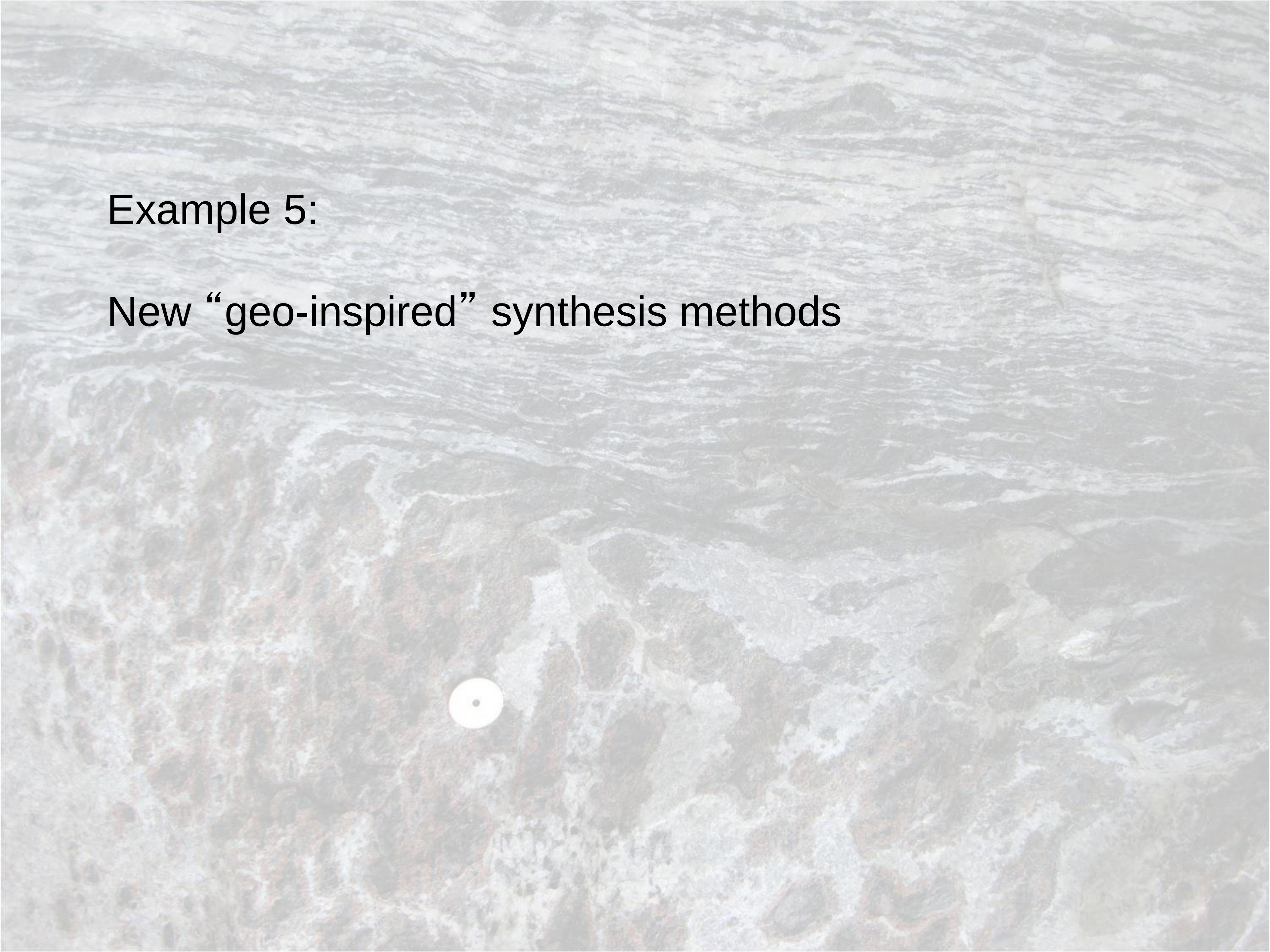
GEOFLUIDS

Geofluids (2010) **10**, 254–269 doi: 10.1111/j.1468-8123.2010.00285.x

Fluid-induced processes: metasomatism and metamorphism

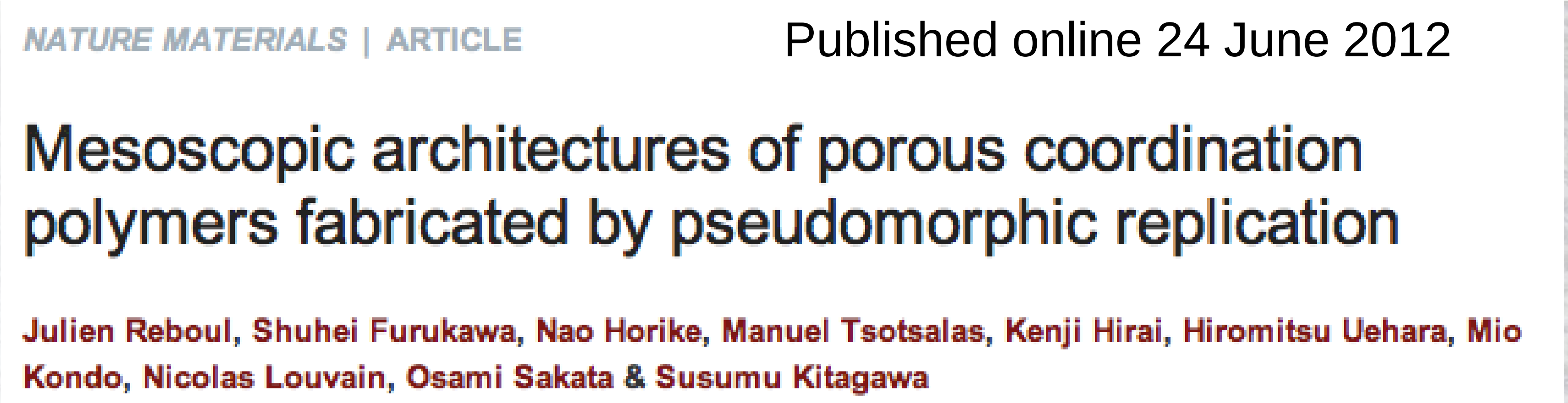
A. PUTNIS[1] AND H. AUSTRHEIM[2]

[1] Institut für Mineralogie, University of Münster, Münster, Germany; [2] Physics of Geological Processes, University of Oslo, Oslo, Norway



Example 5:

New “geo-inspired” synthesis methods



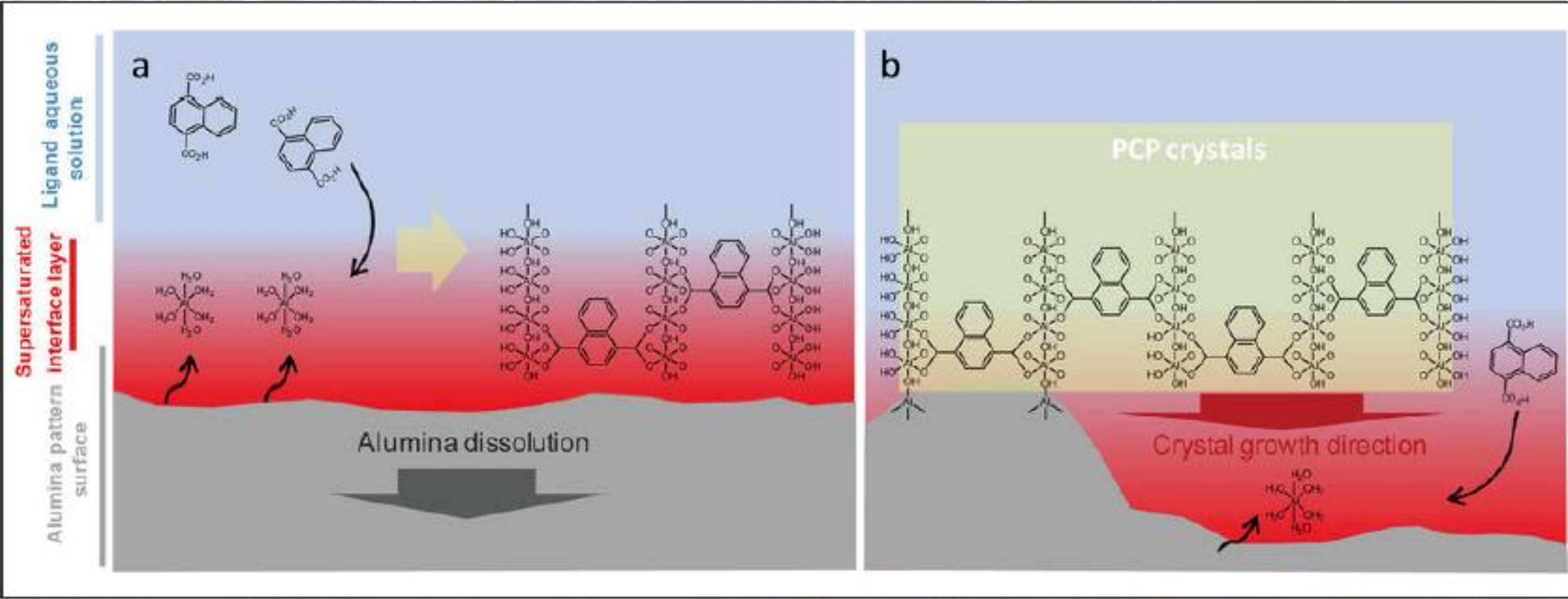
NATURE MATERIALS | ARTICLE

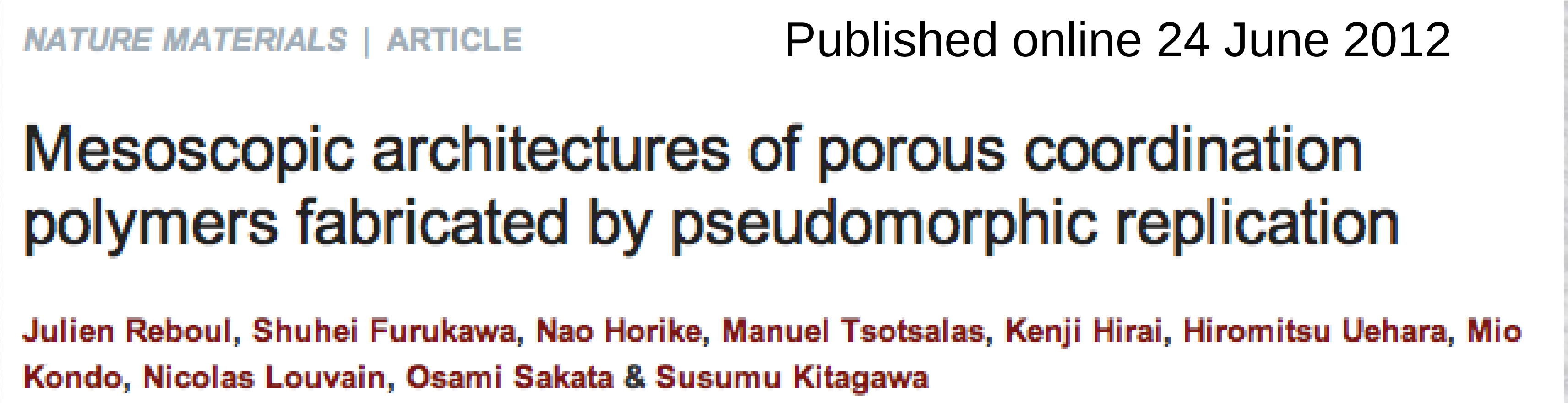
Published online 24 June 2012

Mesoscopic architectures of porous coordination polymers fabricated by pseudomorphic replication

Julien Reboul, Shuhei Furukawa, Nao Horike, Manuel Tsotsalas, Kenji Hirai, Hiromitsu Uehara, Mio Kondo, Nicolas Louvain, Osami Sakata & Susumu Kitagawa

Porous coordination polymers (PCP) e.g. $[Al(OH)(COO)_2]_n$ (aluminium napthalene dicarboxylate) formed by pseudomorphic replacement of alumina using 1,4-naphthalenedicarboxylic acid.





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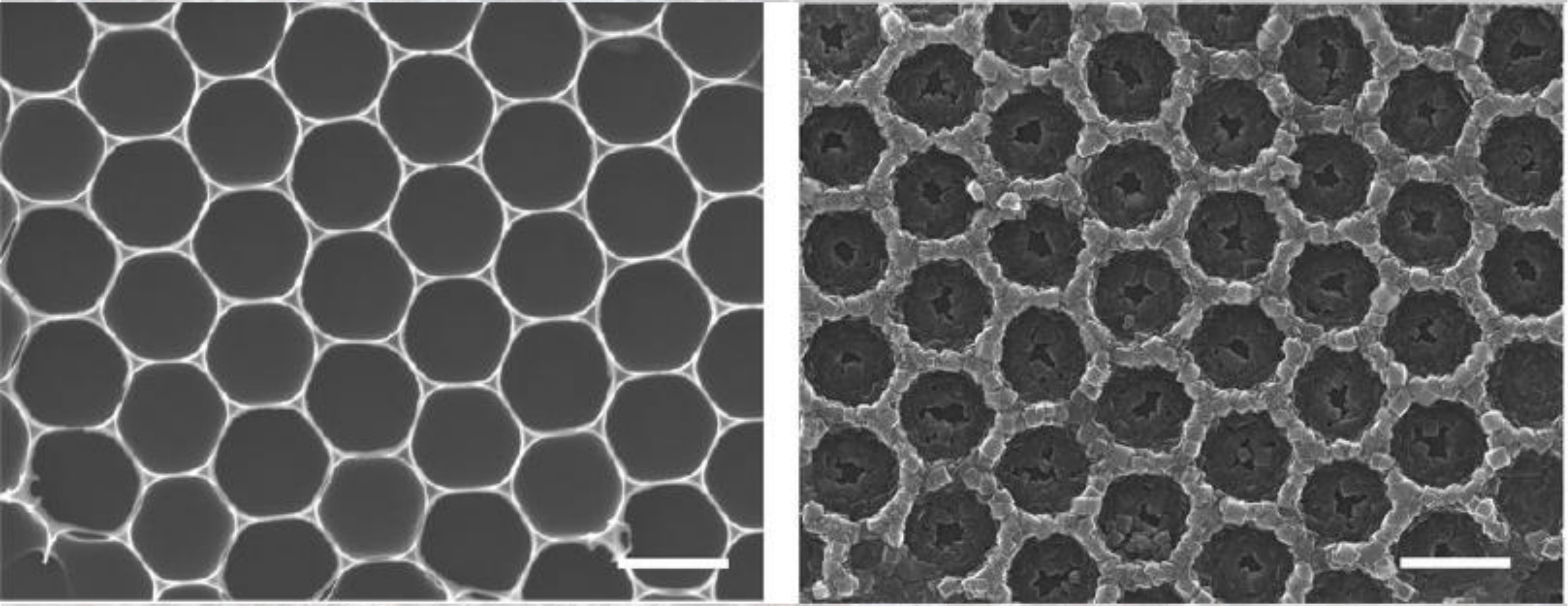
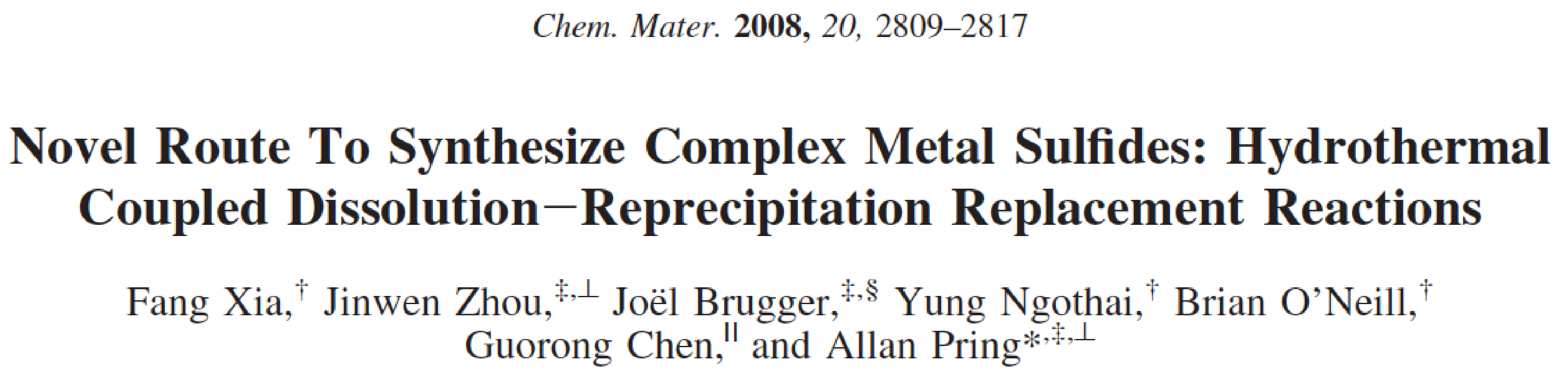
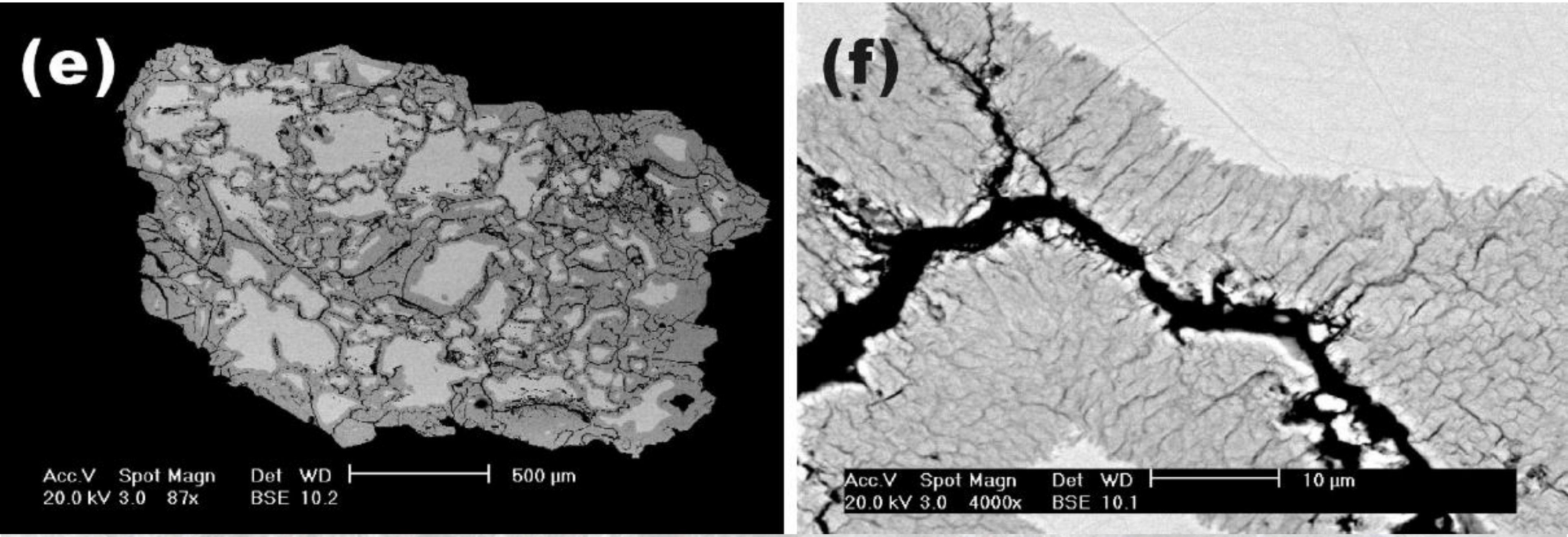




Chem. Mater. **2008,** *20,* 2809–2817

Novel Route To Synthesize Complex Metal Sulfides: Hydrothermal Coupled Dissolution−Reprecipitation Replacement Reactions

Fang Xia,[†] Jinwen Zhou,[‡,⊥] Joël Brugger,[‡,§] Yung Ngothai,[†] Brian O'Neill,[†]
Guorong Chen,[||] and Allan Pring*[,‡,⊥]



Pentlandite $(Fe,Ni)_9S_8$ as the parent phase replaced by violarite $(Fe,Ni)_3S_4$

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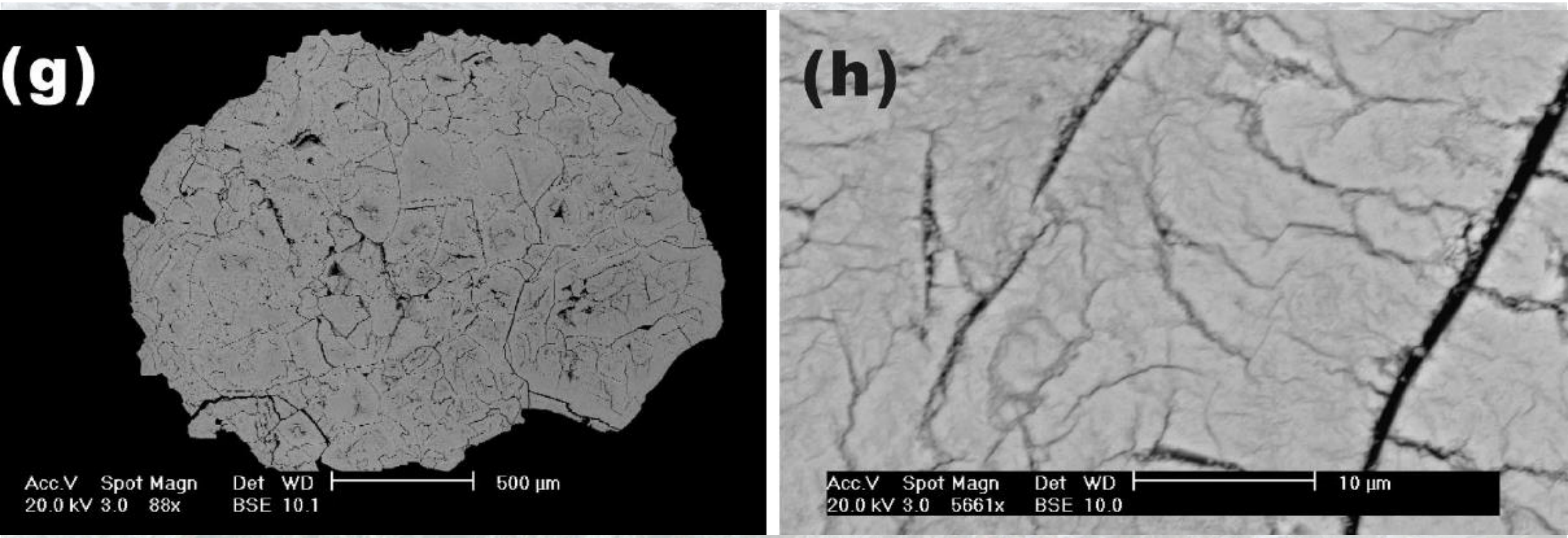
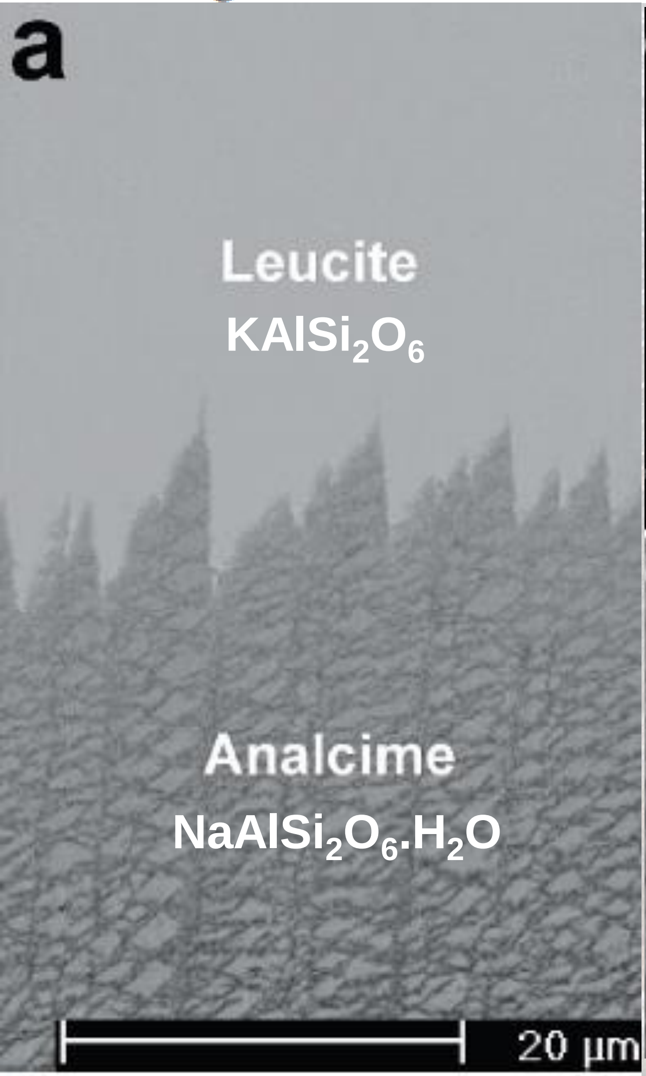


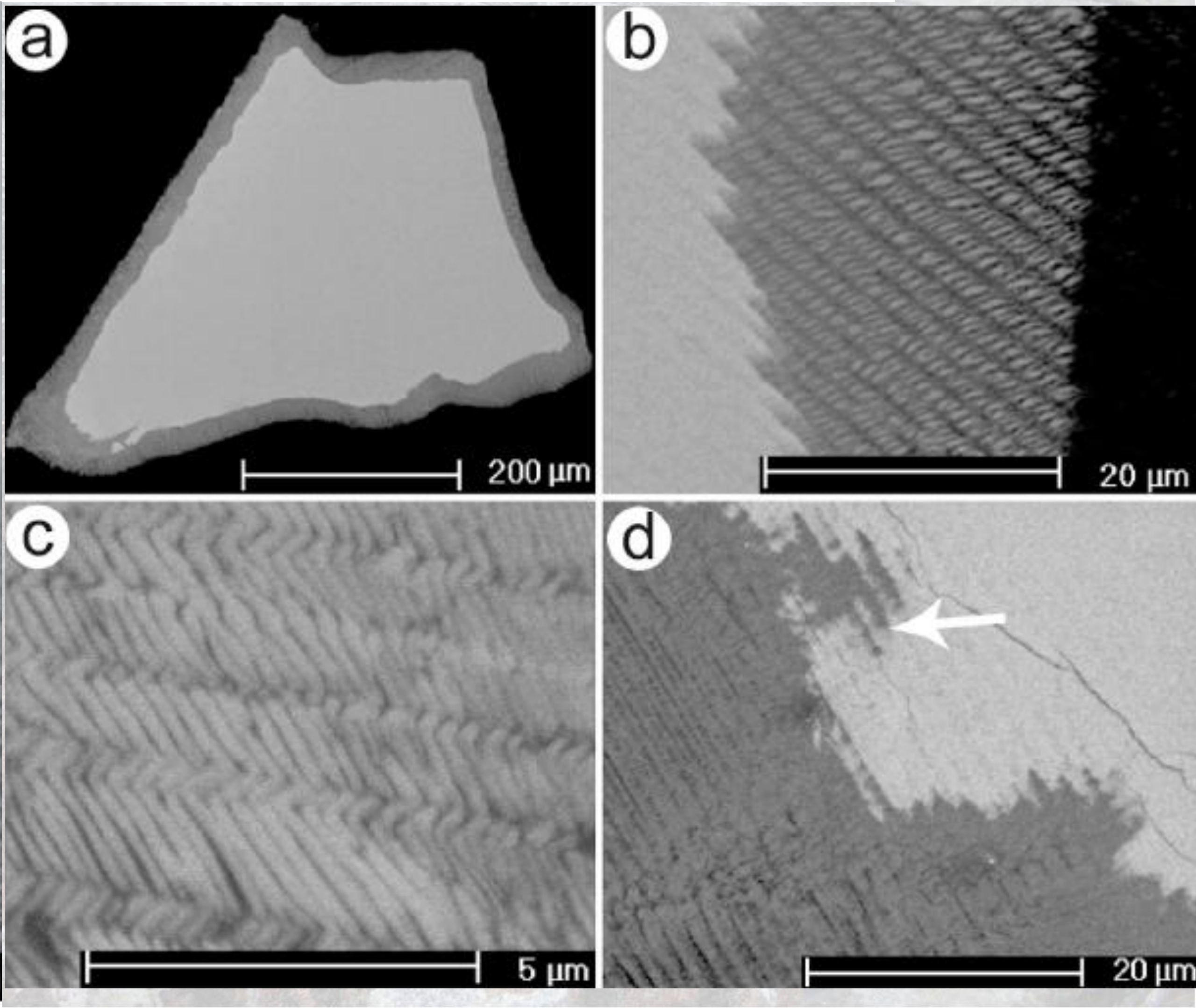
Pentlandite $(Fe,Ni)_9S_8$ as the parent phase replaced by violarite $(Fe,Ni)_3S_4$

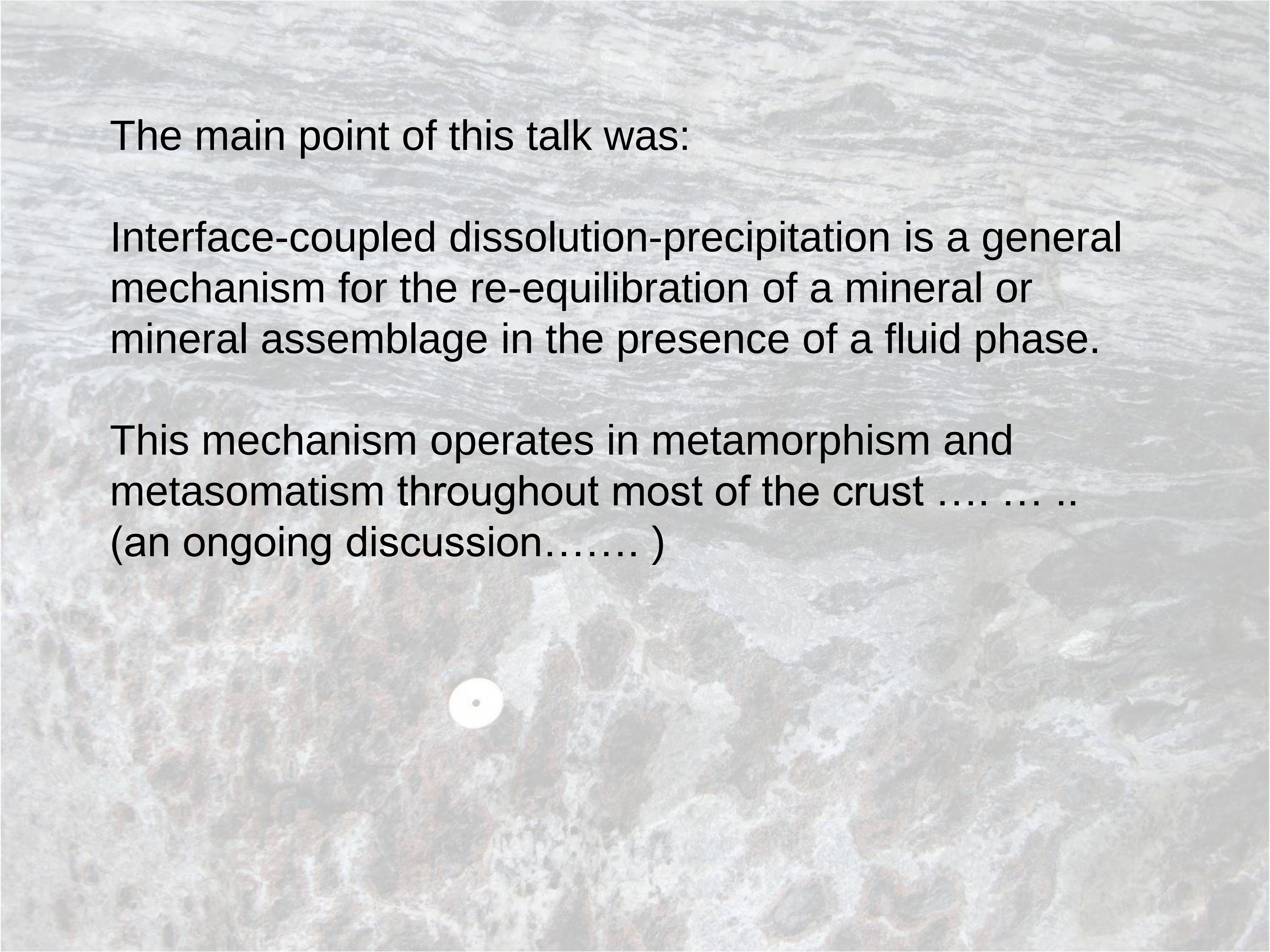
Three-Dimensional Ordered Arrays of Zeolite Nanocrystals with Uniform Size and Orientation by a Pseudomorphic Coupled Dissolution−Reprecipitation Replacement Route

CRYSTAL GROWTH & DESIGN
Article

Fang Xia,*[,†,§] Joël Brugger,[‡,§] Yung Ngothai,[†] Brian O'Neill,[†] Guorong Chen,[‖] a
Allan Pring[‡,§]







The main point of this talk was:

Interface-coupled dissolution-precipitation is a general mechanism for the re-equilibration of a mineral or mineral assemblage in the presence of a fluid phase.

This mechanism operates in metamorphism and metasomatism throughout most of the crust …. … ..
(an ongoing discussion…….)

Acknowledgements:

Collaborators: Encarni Ruiz Agudo, Håkon Austrheim, Thorsten Geisler, Arkady Glikin, Timm John, Helen King.

Students: Laura Jonas, Dominic Niedermeier, Jörn Hövelmann

Funding: European Union Network project:
“Delta-Min” (Mechanisms of Mineral Replacement Reactions)