A "LAB-ON-A-CHIP" EXPERIMENT FOR ASSESSING MINERAL PRECIPITATION PROCESSES IN FRACTURED POROUS MEDIA

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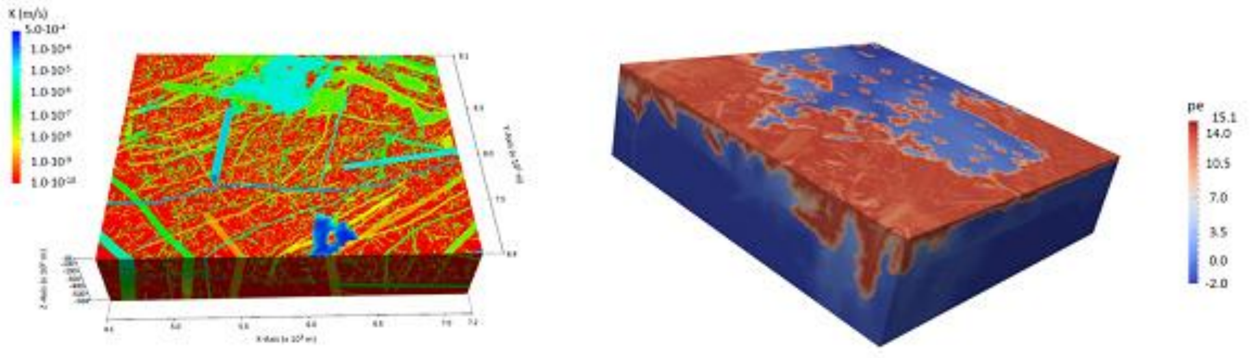
MOTIVATION

- The understanding of chemical changes in fractured porous media is relevant for various subsurface applications: subsurface nuclear waste disposal, fracking, CO_2 sequestration, etc.

- Reactive Transport Modelling can predict chemical reactions along solute transport pathways in space & time

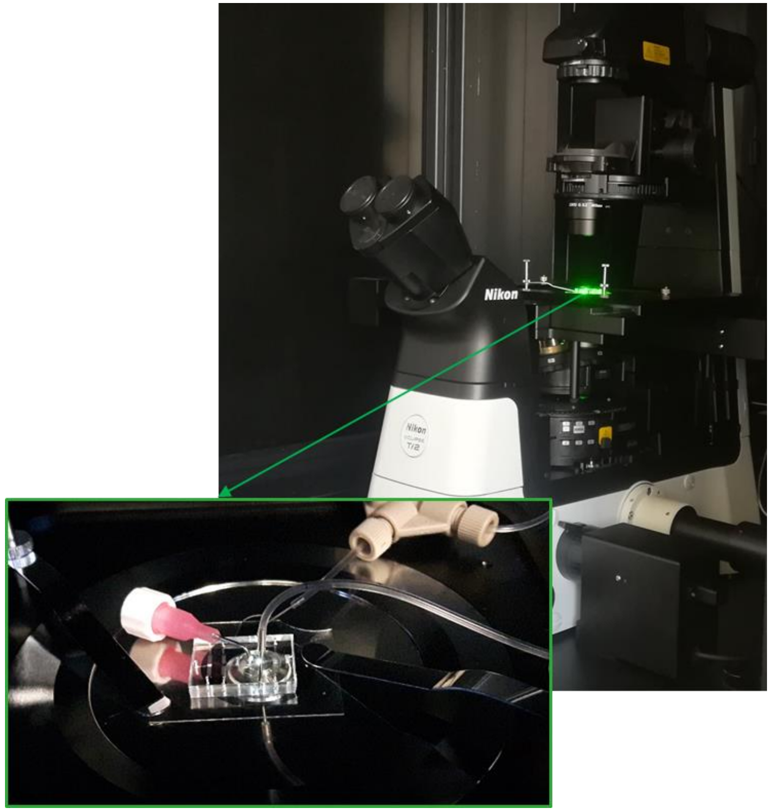
- Challenge: Description of the coupling between chemical processes and changes in material properties. So far, only empirical relationships and parameters are available and used (e.g. evolution of the reactive surface area of minerals)

- Recent experimental benchmarks have suggested the need to understand the processes occurring at the pore-scale and to develop process-based predictive models and mathematical relationships that account for small-scale heterogeneities



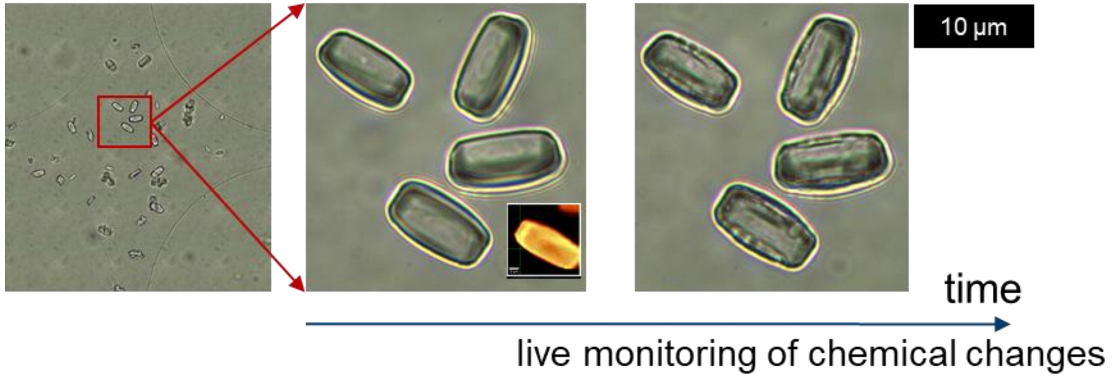
e.g. simulated oxygenated melt water in fractured crystalline porous media in Forsmark site (Sweden) to assess the redox buffering capacity of these host rock formations
Trichinero et al. 2018, DOI:10.1007/s11004-017-9718-6

MICROFLUIDIC EXPERIMENTS



Advantages:

- idealized porous media with controlled pore shape/distribution and mineralogy
- feasibility of constant monitoring
- control on chemical system and environmental parameters (e.g. T)
- coupling with Raman Spectroscopy gives information on the mineralogical changes



→ develop an experiment combined with advance pore scale modelling to understand the physics of precipitation/dissolution processes in fractured porous media

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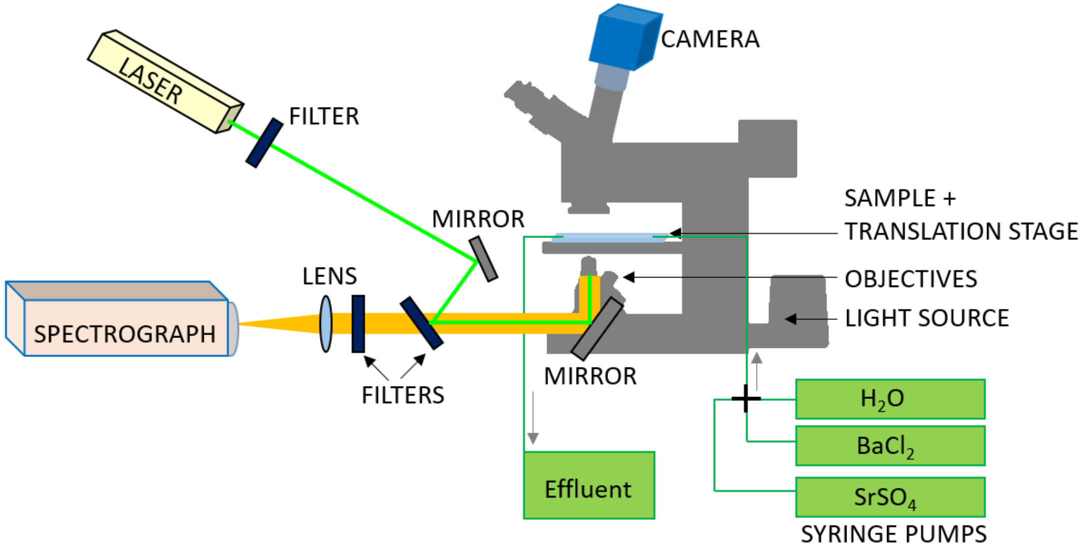
EXPERIMENTAL SET-UP

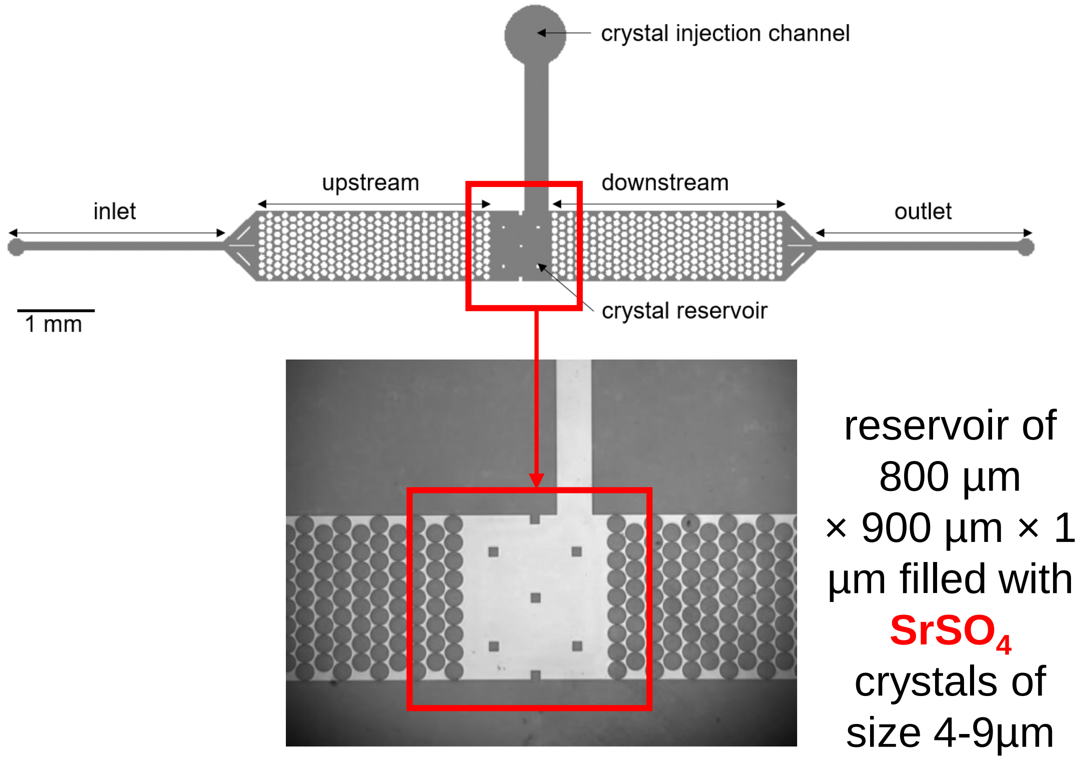
Microfluidic combined with raman spectroscopy



- injection of a reacting solution of $BaCl_2$ at a constant flowrate in the microreactor

$BaCl_{2(aq)} + SrSO_{4(s)} \rightarrow BaSO_{4(s)} + SrCl_{2(aq)}$

Microfluidic reactor design



reservoir of 800 µm × 900 µm × 1 µm filled with $SrSO_4$ crystals of size 4-9µm

- chip manufactured by conventional pdms techniques and closed with glass

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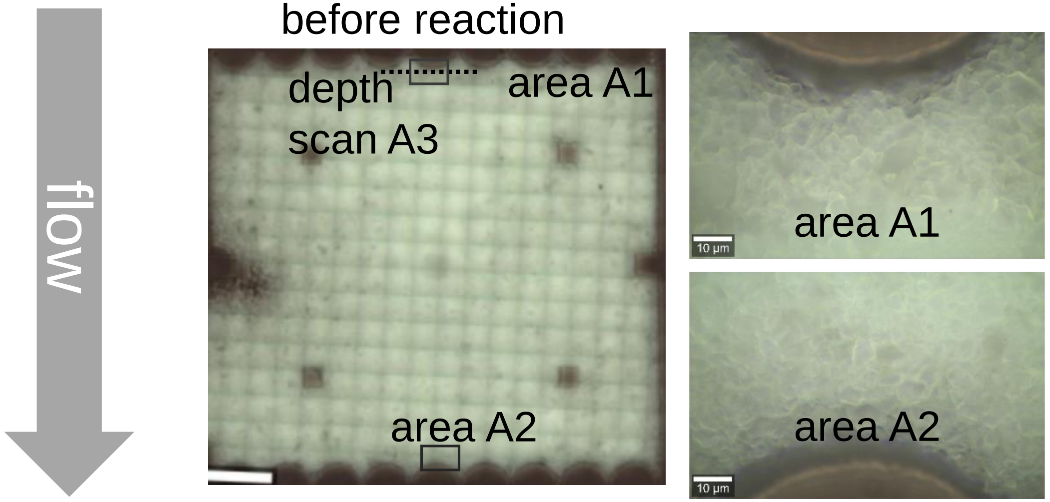
COMPACTED POROUS MEDIA

Porous media generated with this technique can be either homogeneous or heterogeneous

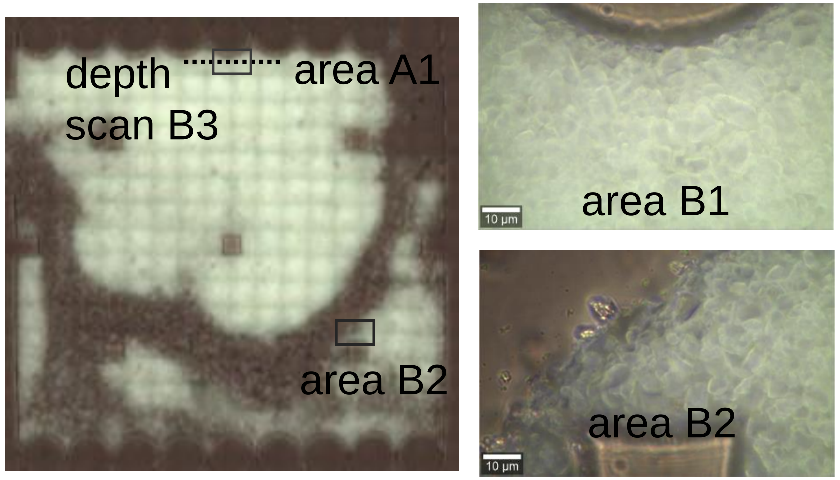
- Homogeneous porous media

before reaction



- Heterogeneous(fractured) porous media

before reaction



- Raman map of selected areas A1, A2, B1 and B2 were collected at regular interval of times
- Raman depth scan and a raman tomograph were collected before and after chemical reactions

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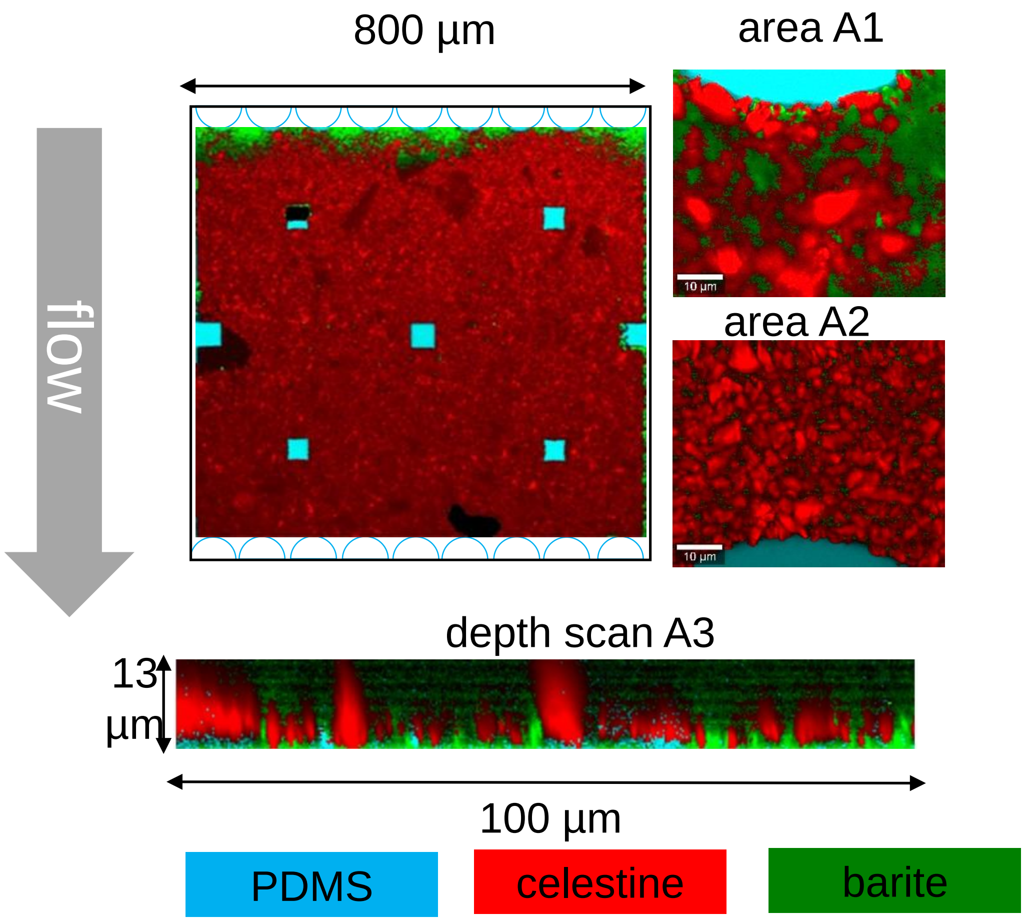
MINEROLOGICAL CHANGES

Raman map of the homogeneous porous media after reaction



- Barite precipitated

- along 50µm in the upstream section
- in between the celesine crystals downstream

- A considerable amount of celesine is still present in the system

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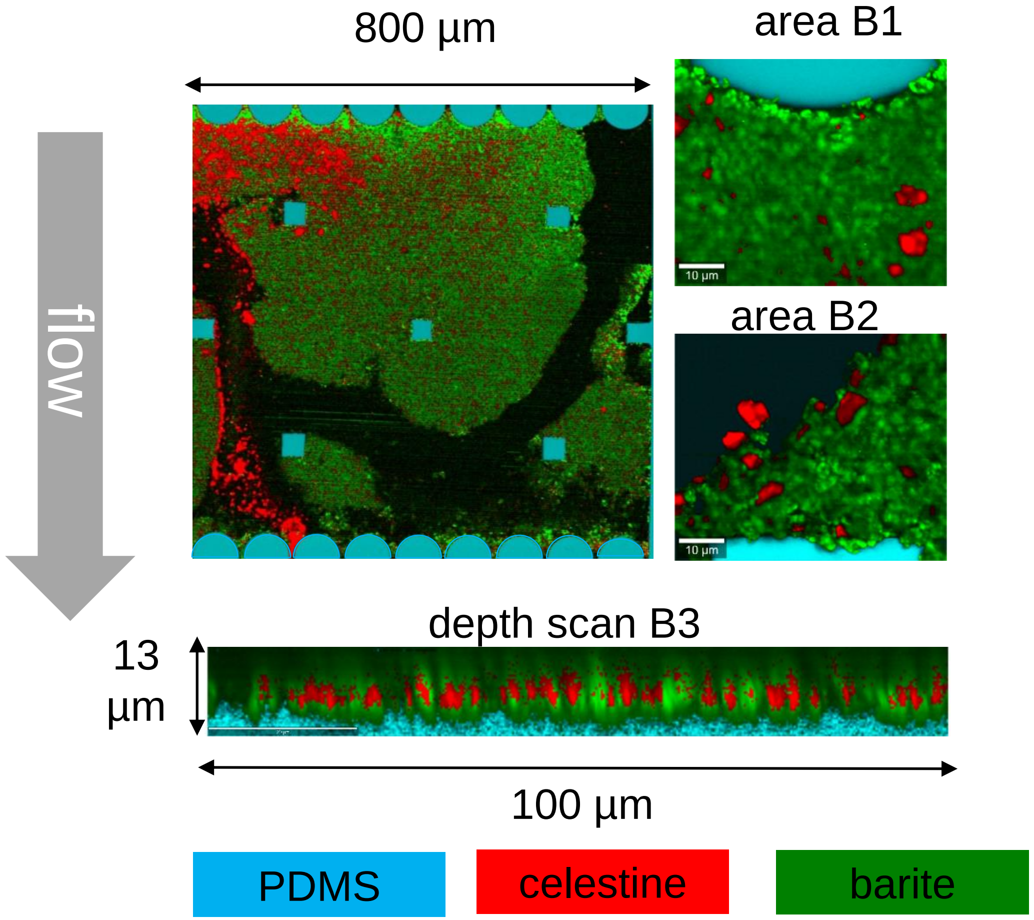
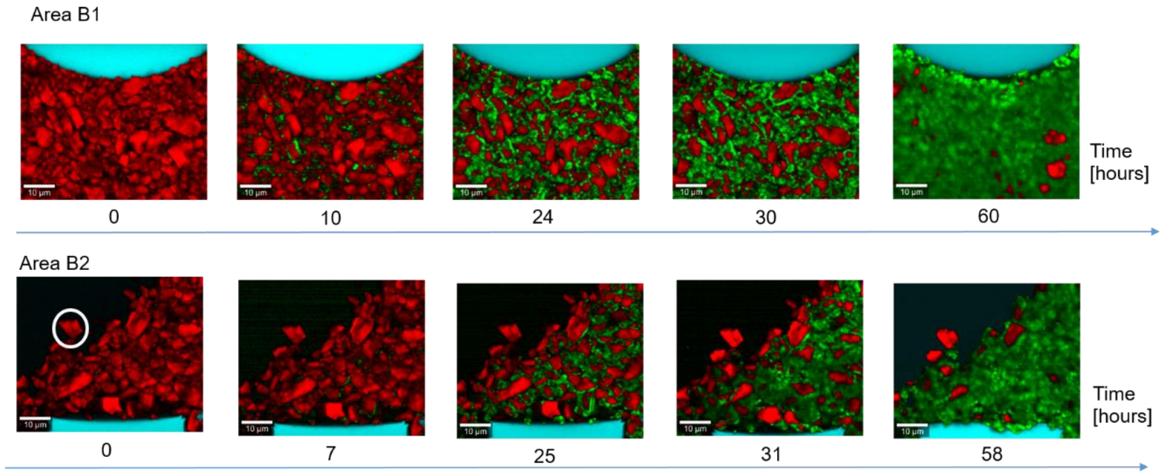
MINEROLOGICAL CHANGES

Raman map of the heterogeneous porous media after reaction





- Barite precipitated mainly across the main flow path
- Barite nucleation appears to start on the step like features of the individual celestine crystals (epitaxial growth)
- Celestine is present in the left side of the reservoir
- Crystals directly adjacent to the fracture undergo dissolution

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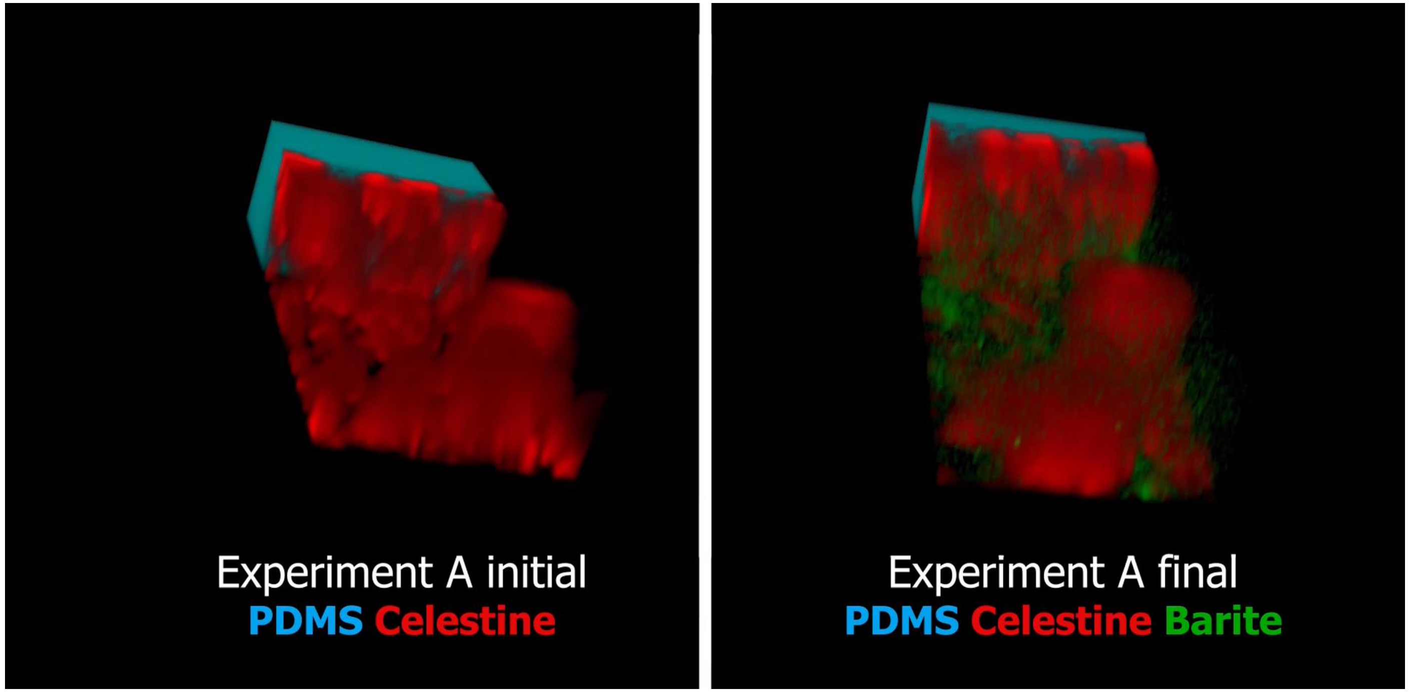
RAMAN TOMOGRAPHY

3D representation of the porous media before and after reaction



- 3D tomograph enables the evaluation of porosity, mineral mole fraction, and dissolution rates

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RAMAN TOMOGRAPHY

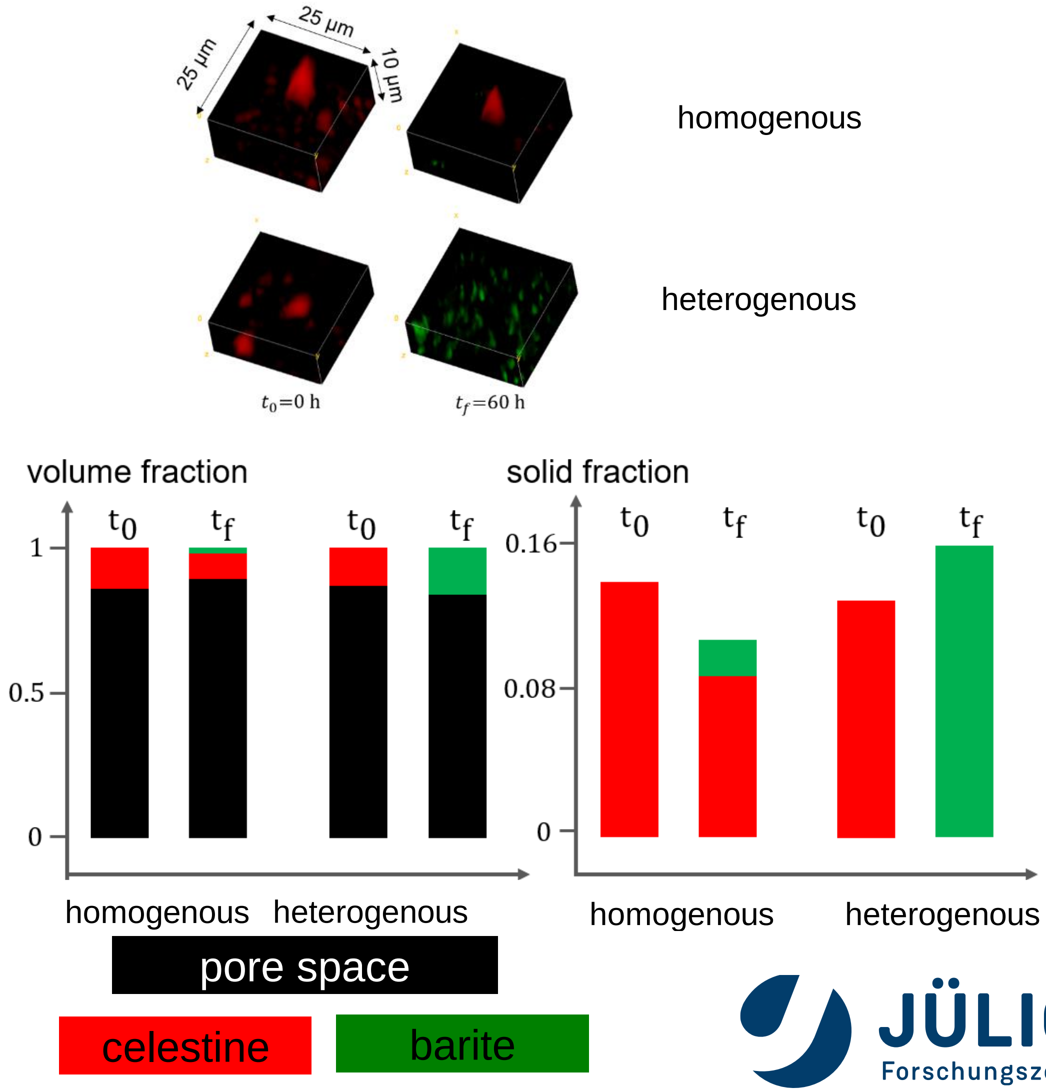
Evaluation of the mineral amounts in the systems

Homogeneous case:
Porosity increase suggesting that dissoluton is faster than precipitation

Heterogeneous case:
Porosity decrease. Complete conversion of celestine to barite

The amount of barite that precipitated in the heterogenous compacted porous media is more than that that precipitated in the homogeneous porous media.

How to explain the differences in minerological changes?



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EVALUATION OF VELOCITY FIELDS

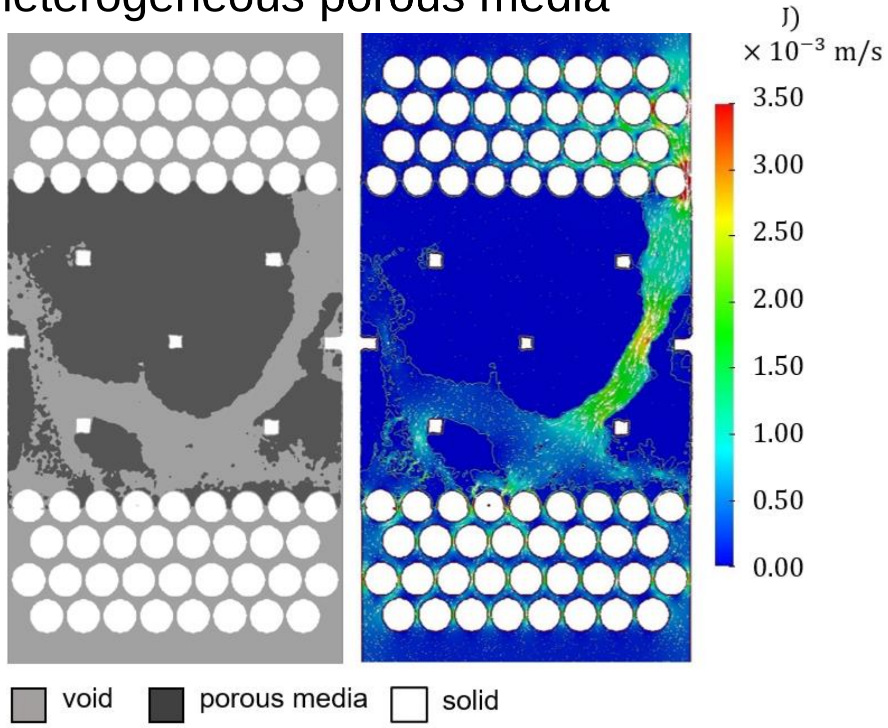
Simulated velocities

Homogeneous case:
velocity in the compacted regions: 9.25×10^{-4} ms^{-1}
Pe numbers 4.65→advection dominates

Heterogeneous case:
velocity along the fractures evaluated 3.5×10^{-3}
velocity in the compacted regions: 4×10^{-5} ms^{-1}
Pe number compacted region 0.25→diffusion dominates

- Velocity in compacted homogeneous porous media is 19 times higher than in the compacted fractured media

Simulated velocity fields for heterogeneous porous media



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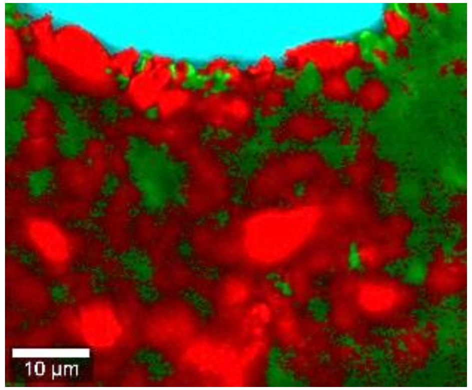
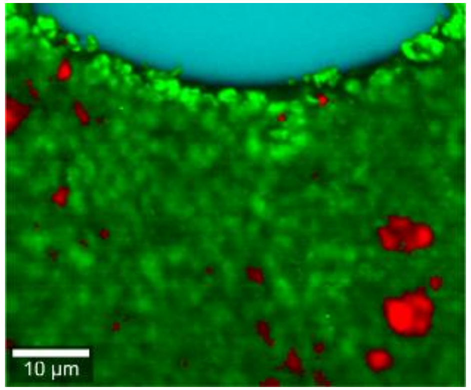
HOW TO EXPLAIN THE DIFFERENCES IN MINEROLOGICAL CHANGES?

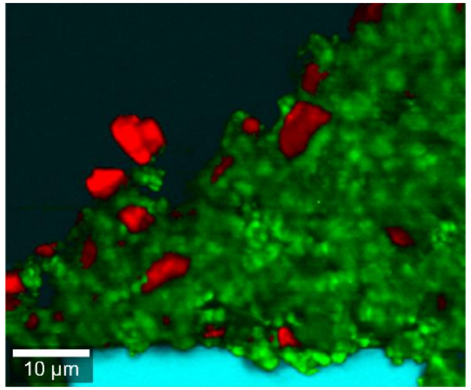
Homogeneous case



- High velocities translate to high Pe numbers, and short residence time
- Incoming solution is undersaturated w.r.t to celestine that drive its dissolution
- Insufficient time for barite to nucleate on the surface of celestine
- Dissolution is faster than precipitation→ porosity increase

Heterogenous case





- In the compacted regions
  - Low velocities translate to low Pe numbers, and longer residence time
  - Ample time for barite to nucleate and precipitate as Sr^{2+} is released into the pore solution during celestine dissolution
- Along the fracture, velocity is higher, shorter residence time and consequently not enough time for barite to nucleate

➢ The velocity field has an impact on the residence time and consequently on the precipitation

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CONCLUSIONS AND OUTLOOK

- Establishment of a new flow-through microfluidic reactor coupled with high-resolution imaging that enables in situ and non destructive 3D assessment of mineralogical and microstructural changes with full spatio-temporal resolution on the grain scale

- This methodology allows a systematic study of the chemical and porosity evolution of the system at the pore-scale

- Future work:

The in-situ 3D Raman reconstruction of the pore architecture along with advanced pore-scale modelling will provide a better assessment of the transport properties (e.g. permeability, dispersion tensor) as well as the accessible reactive surface area and reaction rates for describing mineral precipitation/dissolution in porous media.

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