Investigation of mineral reactivity in CO_2 -bearing solutions

DESTRESS Mid-Term Conference

Jin MA

Participants:

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Outline

- Background
- Sample characterization
- Reactive flow-through experiment
- Conclusions and future work

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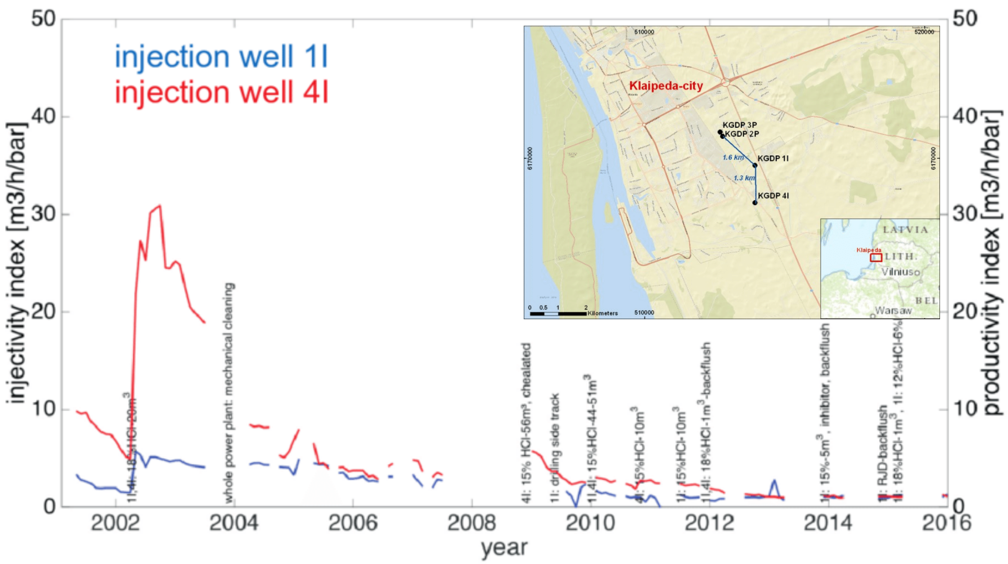
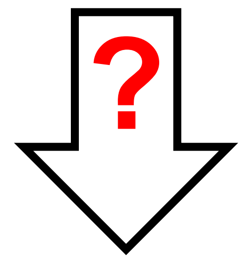
Background: motivation

Granite sample from EPS 1 Soultz, France



Injectivity index in Klaipeda, Source: Maren Brehme et al., 2017

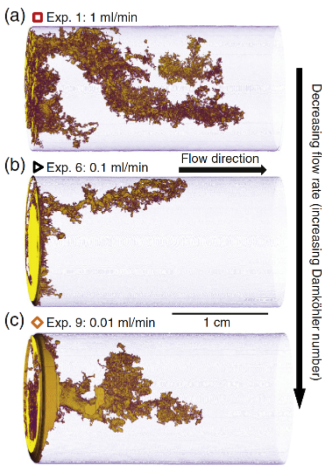
Mineral precipitation



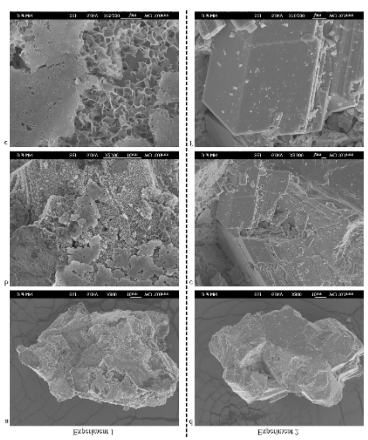
Injectivity reduction

Background: fluid-rock reactions

Mineral dissolution / precipitation



Luhmann et al., 2014



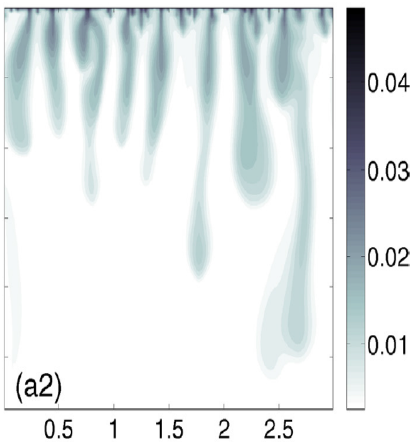
Luhmann et al., 2013

Property alterations

- Pore structure
- Pore size distribution
- Porosity
- Permeability
- Flow field
- Accessible surface area
- Reaction rates
- Reservoir productivity/injectivity

Background: an exploration with CO_2 ?

CO_2 dissolution



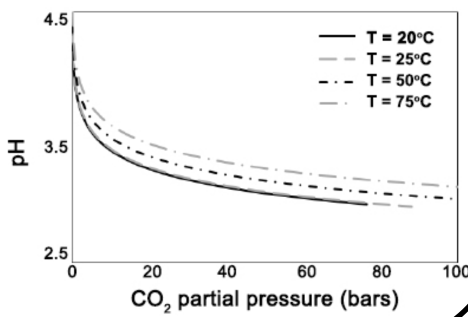
CO_2 dissolution
Kong and Saar, 2013

$$CO_2(g) \xleftrightarrow{Dissolution} CO_2(aq)$$

$$CO_2(aq) + H_2O \xleftrightarrow{K=1.3\times10^{-3}} H_2CO_3$$

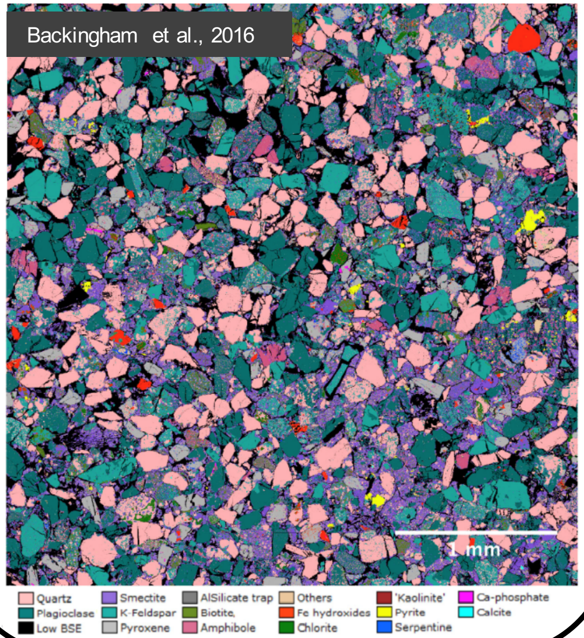
$$H_2CO_3 \xleftrightarrow{K=2\times10^{-4}} H^+ + HCO_3^-$$

$$HCO_3^- \xleftrightarrow{K=4.69\times10^{-11}} H^+ + CO_3^{2-}$$



+

Multiple minerals

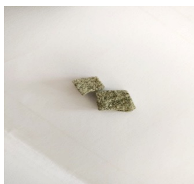


Mineral reactivity in CO_2-bearing solutions

Outline

- Background
- Sample characterization
  - Mineralogy analysis
  - Effective surface area estimation
- Reactive flow-through experiment
- Conclusions and future work

Sample characterization: Laboratory measurements



Piece

- Hg porosimetry
- BET
- 3D μCT (~1 μm)

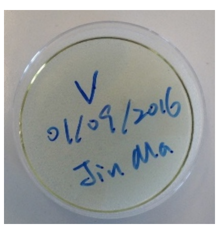
Vydmantai Lithuania

Core

- Flow-through experiments
- Porosity
- 3D μCT (~10 μm)

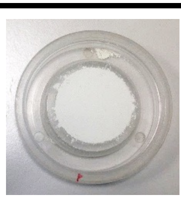
Fusion bead

- X-ray fluorescence (XRF)



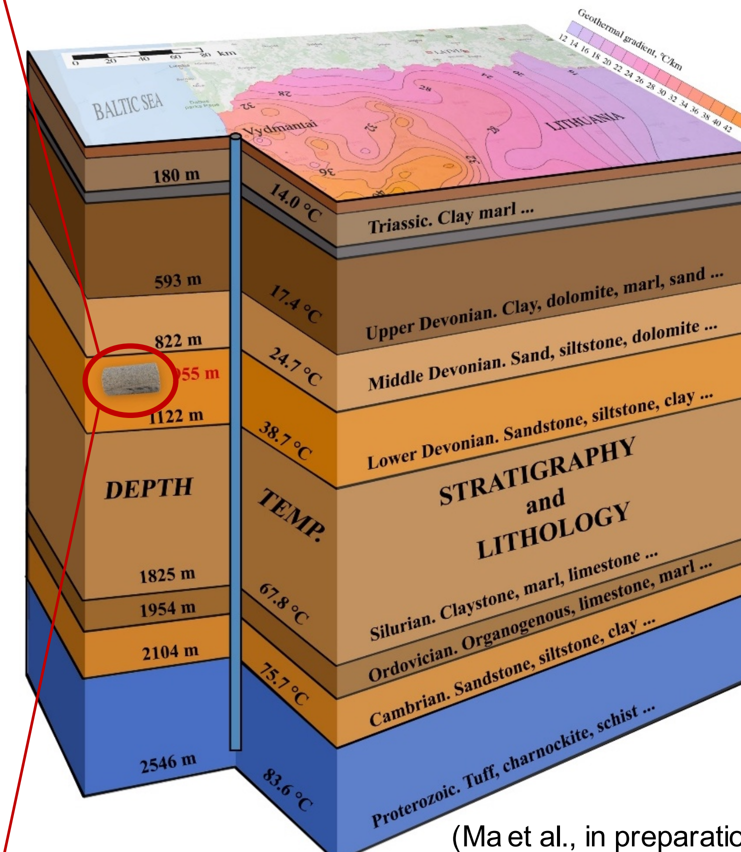
35 μm thin section

- Microscopy
- SEM-BSE/EDS image



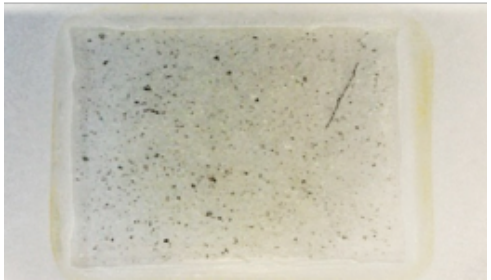
Fine powder

- X-ray powder diffraction (XRD)

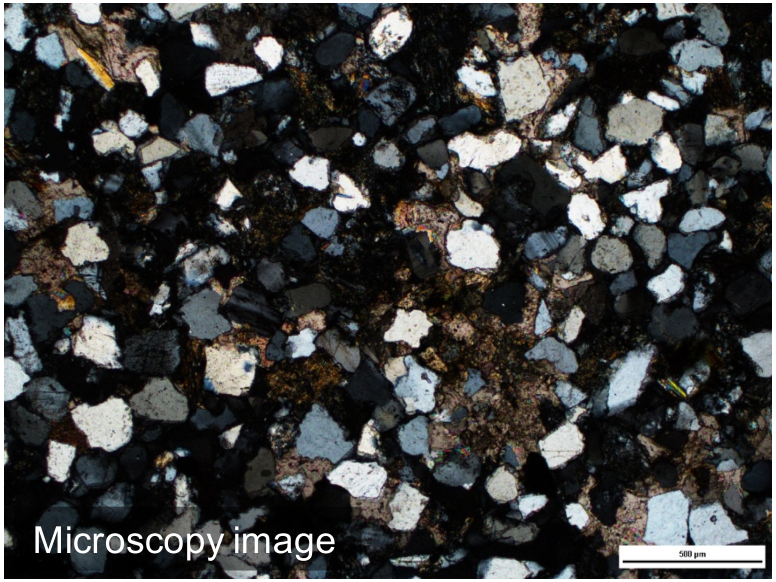


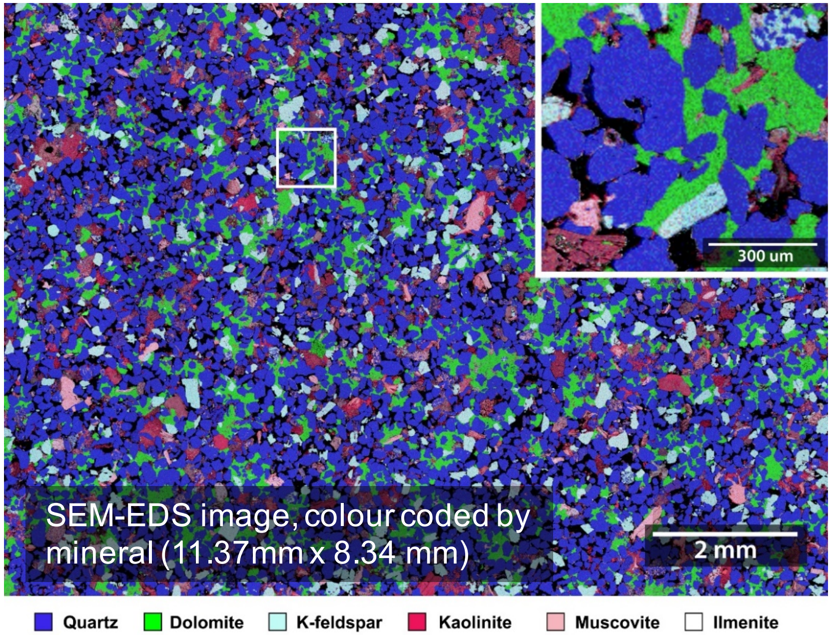
(Ma et al., in preparation)

Sample characterization: mineralogy analysis



Thin section: 2.8 cm x 2.2 cm





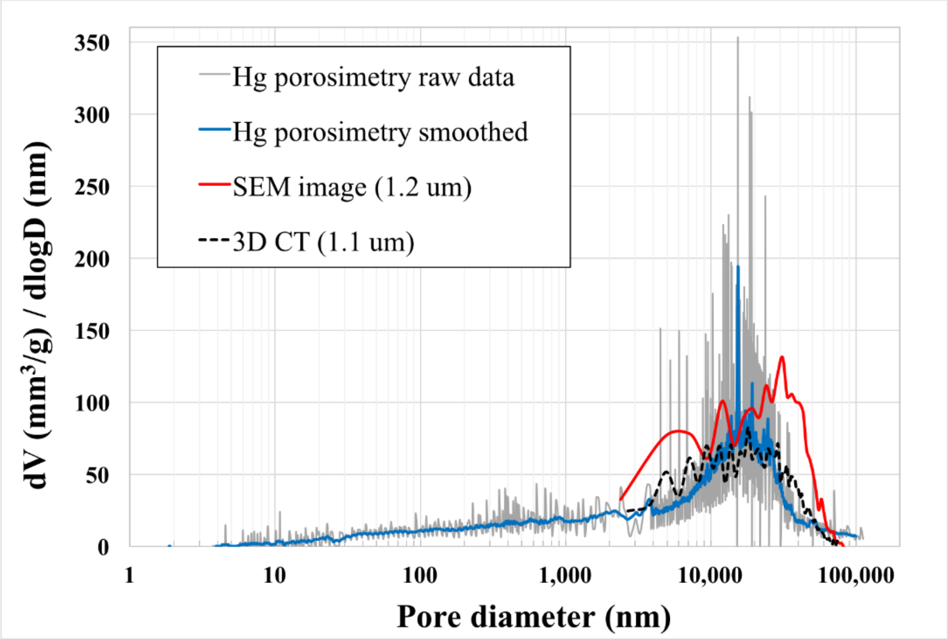
(Ma et al., in preparation)

Mineral	Average chemical formula	XRF+XRD vol.%	SEM vol. %
Quartz	SiO_2	47.65	45.53
Dolomite	$CaMg_{0.77}Fe_{0.23}(CO3)_2$	12.36	12.22
K-feldspar	$KAlSi_3O_8$	11.82	9.93
Muscovite	$K_{0.85}Na_{0.15}Al_2(AlSi_3O_{10})(OH)_2$	5.38	4.76
Kaolinite	$Al_{1.9}Si_{2.1}O_5(OH)_4$	0.91	5.64
Ilmenite	$Fe_2Ti_5O_{12}$	0.23	0.27

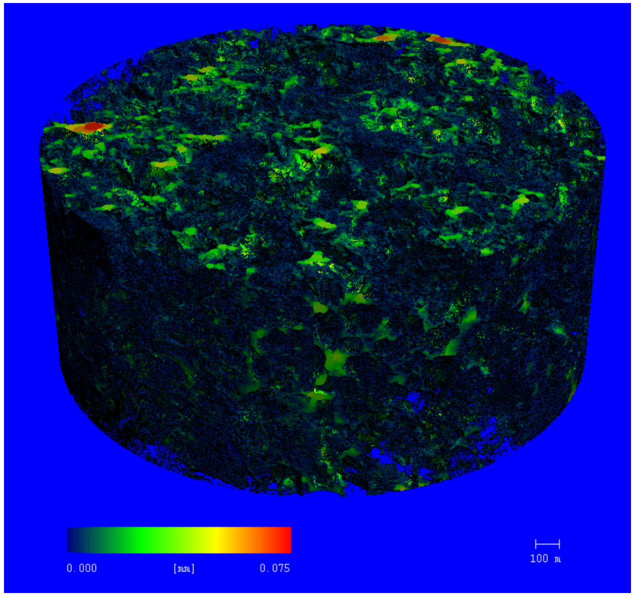
Sample characterization: Stereological bias

- ✓ **Porosity:** - Helium pycnometry: 21.9%
  - SEM-BSE image: 21.7%

- ✓ **Pore size distribution**



(Ma et al., in preparation)

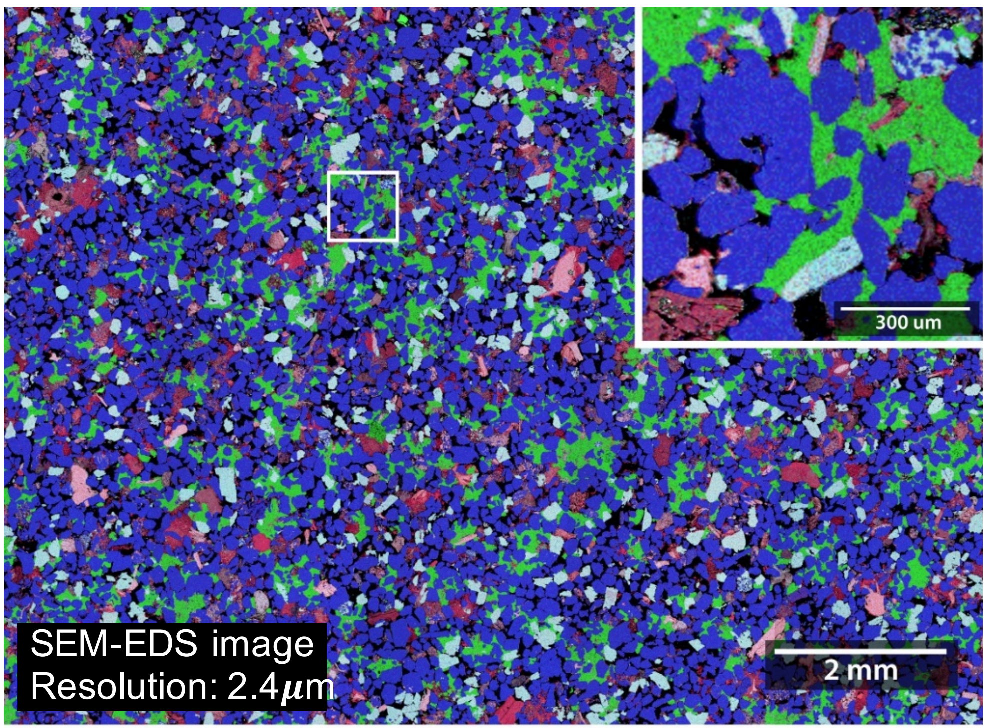


Pore size distribution analysis from 3D CT image (1.1 μm)

Sample characterization: surface area estimation

✓ **Specific surface area (SSA)**

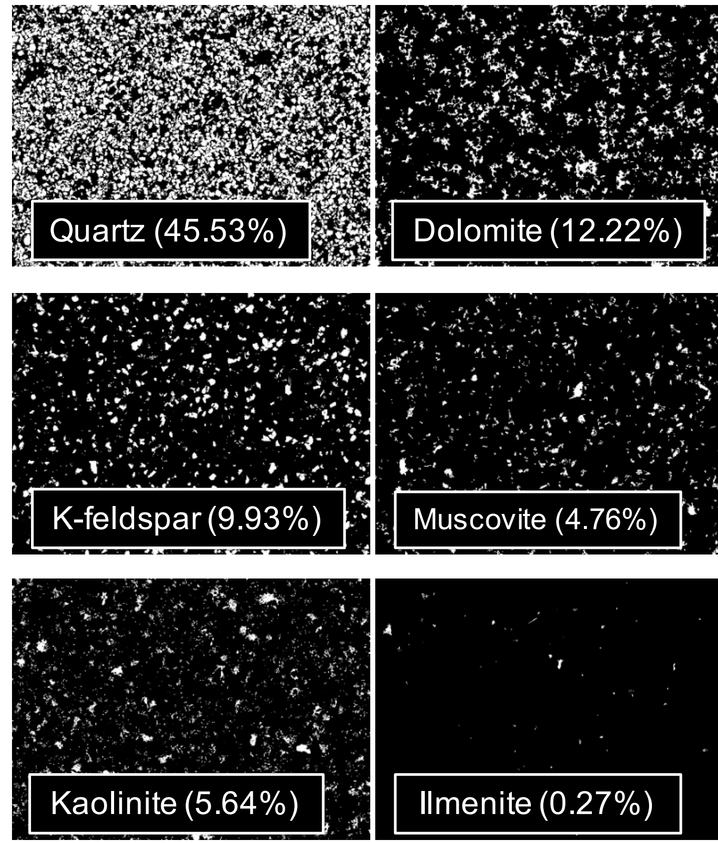
- BET (N_2@77.3K): 1.447 m^2/g
- SEM-BSE image: 0.031 m^2/g



Quartz Dolomite K-feldspar Kaolinite Muscovite Ilmenite

(Ma et al., in preparation)

Surface roughness?



Sample characterization

Mineral	Chemical formula	Volume fraction (%)	Effective surface area (m^2/g)
Quartz	SiO_2	45.53	0.07
Dolomite	$Ca_{1.05}Mg_{0.75}Fe_{0.2}(CO_3)_2$	12.22	0.06
K-feldspar	$KAlSi_3O_8$	9.93	0.01
Muscovite	$K_{0.5}MgFe_{0.4}Al_{1.2}(AlSi_3O_{10})(OH)_2$	4.76	0.06
Kaolinite	$Al_{1.8}Si_{2.2}O_5(OH)_4$	5.64	1.24
Ilmenite	$Ti_5Fe_2O_{12}$	0.27	0.005

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  - Permeability evolution
  - Dolomite dissolution
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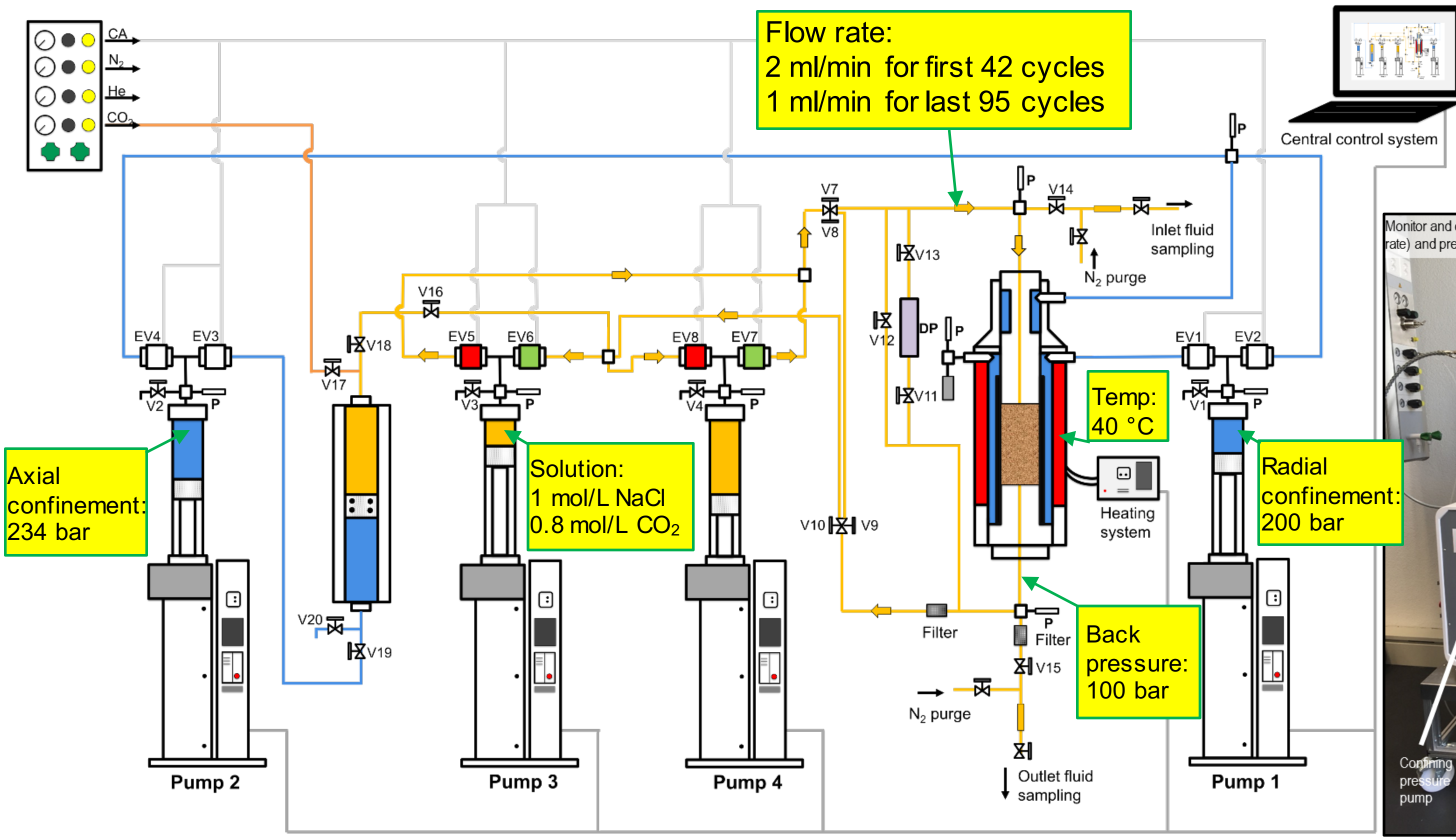
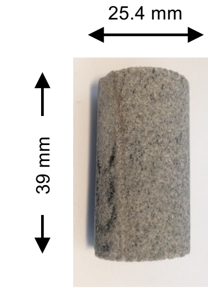
Reactive experiment: set-up

Recycling (RC) experiment: approaching equilibrium

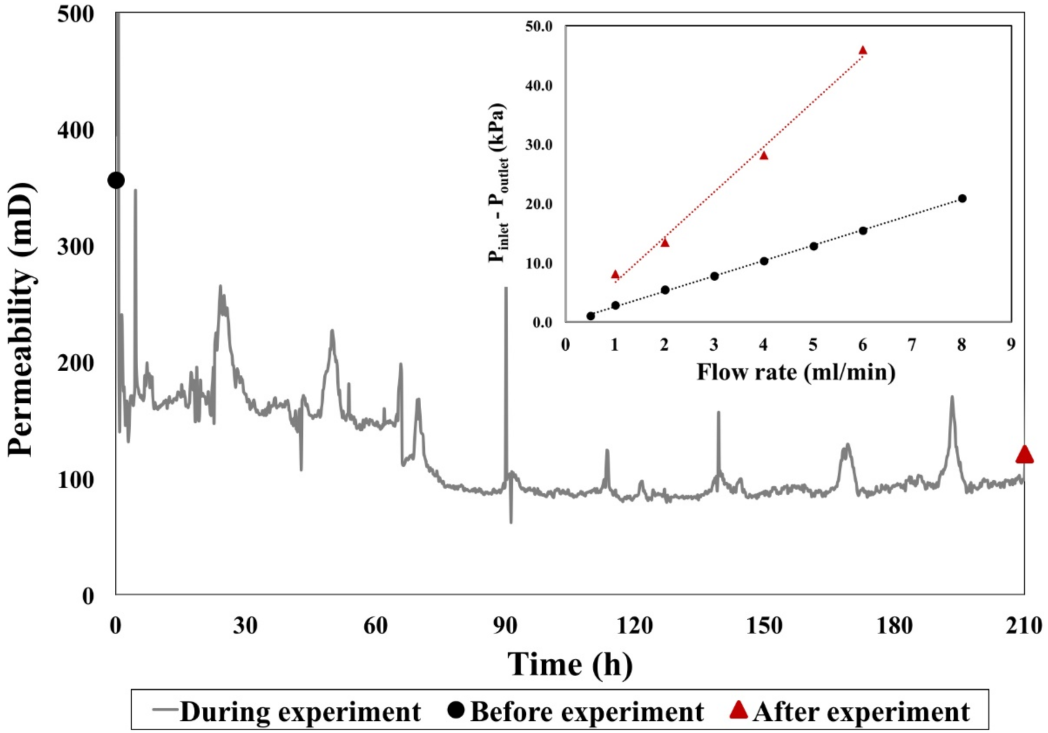




Duration: 10 days
Total cycles: 137
Total recycled volume: 16.7L

Reactive experiments: permeability evolution

Darcy's law: $k = Q\boldsymbol{\mu} L / A \, \Delta P$



(Ma et al., in preparation)

After reaction:

Porosity: 22% ⟶ 25%

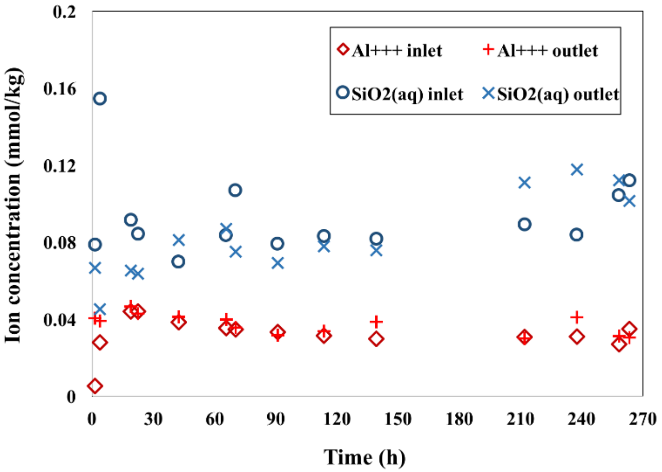
Permeability: 356 mD ⟶ 121 mD

Pore volume increase: 0.674 ml

Total dissolved mass: 0.559 g

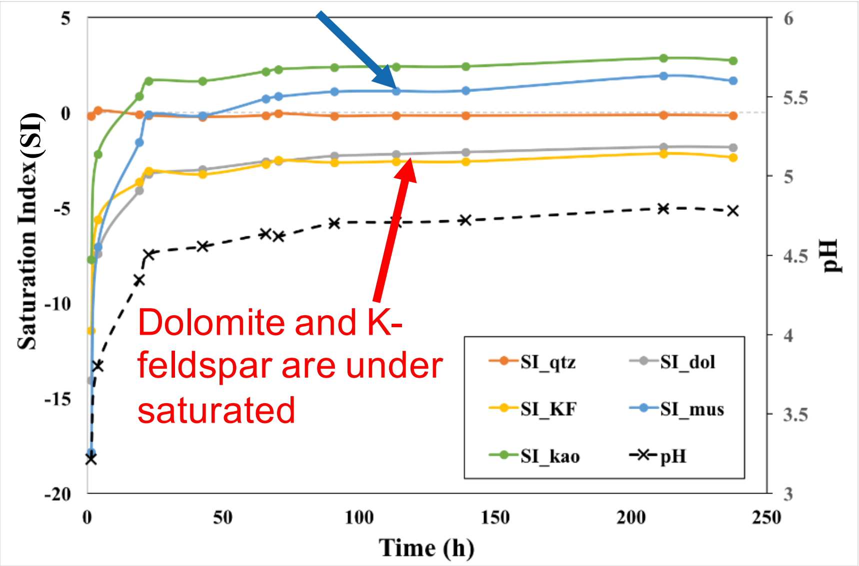
$\frac{\text{Dissolved dolomite}}{\text{Total dolomite}}$: 8%

Reactive experiments: mineral saturation state



Mineral saturation indices of inlet fluid sample, calculated using Geochemist's Workbench:

Kaolinite and muscovite are over saturated



(Ma et al., in preparation)

Negligible precipitation:

- Dolomite and K-feldspar are under-saturated.
- Chemical simulations imply that kaolinite is more likely to precipitate than muscovite. Once kaolinite precipitates, muscovite will become under-saturated.
- Al+++ and SiO_2(aq) concentrations stabilize quickly.
- No obvious Al+++ and SiO_2(aq) concentration difference between the inlet and outlet fluids.
- Estimated maximum kaolinite precipitation: 0.012 ml ≈ 0.27% porosity decrease.

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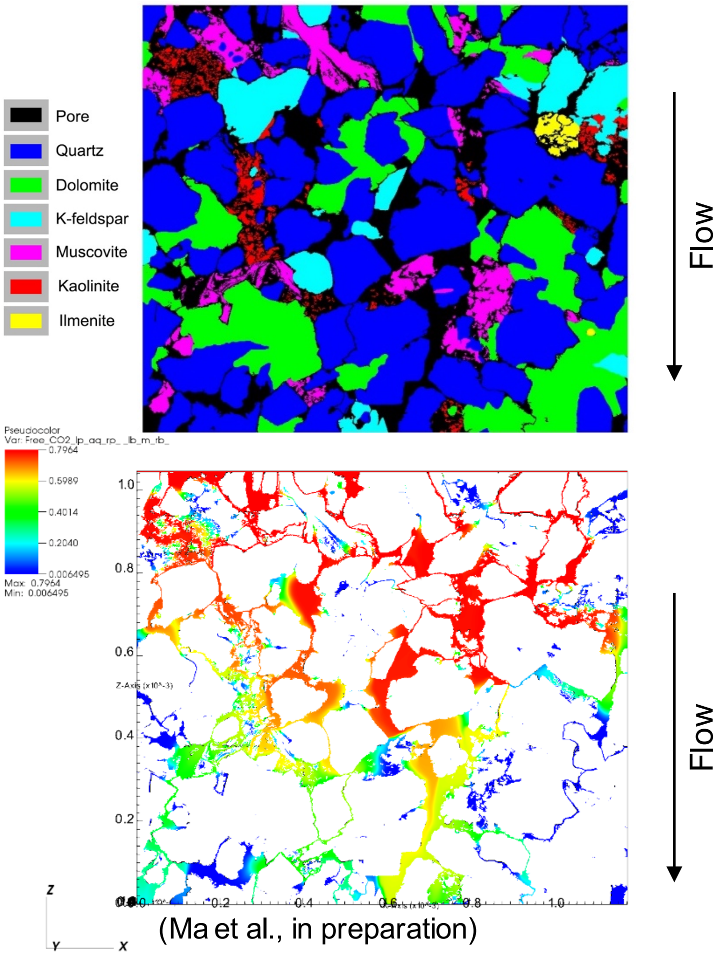
Conclusions and future work

- Dolomite dissolution leads to porosity increase.
- However, permeability decreased during the reaction. Due to fine migration? But we did not find any particles in our outlet filter.
- Our chemical results indicate negligible mineral precipitation.
- Pore volume increase is more than the volume of dissolved dolomite, suggesting that 'isolated pores' became accessible due to dissolution.

Pore-scale reactive simulation



(Ma et al., in preparation)

Thank you!