Storing CO_2 in volcanic rocks: insights from reactive flow-through experiments coupled with multi-scale imaging techniques

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Stanford University
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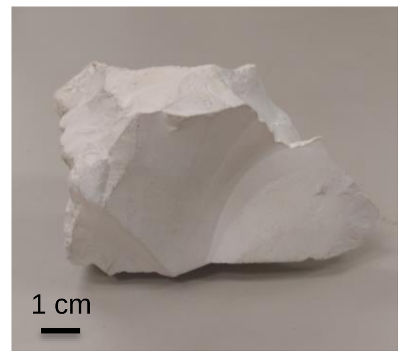
Carbonate mineralization is a safe, long-term and effective storage mechanism

basalt

calcite, $CaCO_3$



magnesite, $MgCO_3$

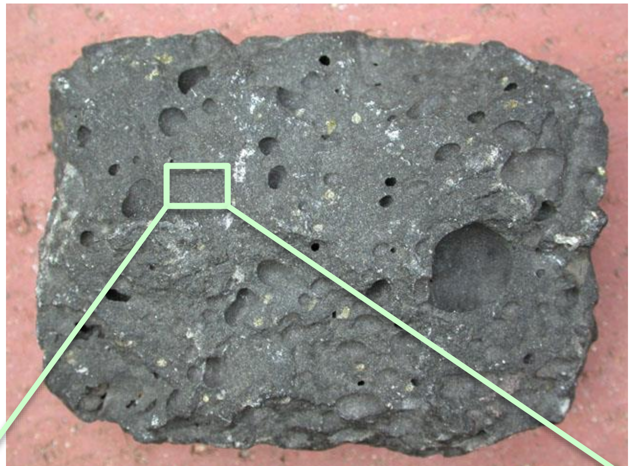
siderite, $FeCO_3$

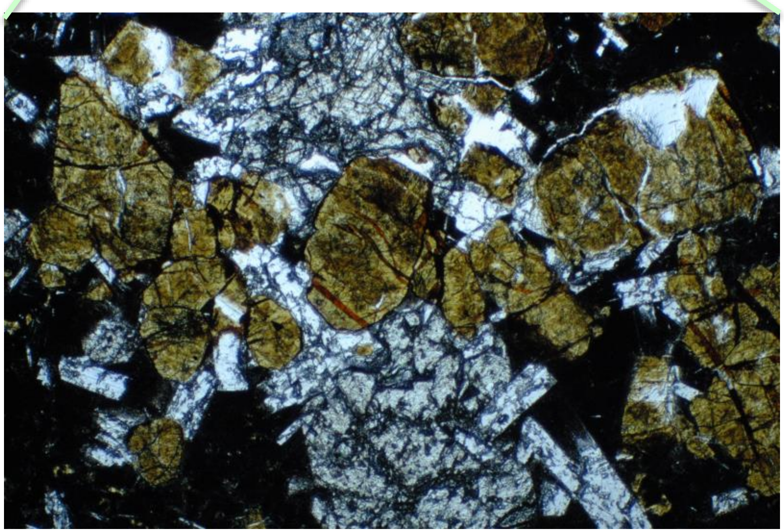
$$CO_2 + H_2O \rightarrow H^+ + HCO_3- \rightarrow HCO_3- + CO_3^{2-}$$

$$\text{Ca-Mg-Fe-silicate} + H^+ \rightarrow Ca^{2+}, Mg^{2+}, Fe^{2+}$$

$$Ca^{2+}, Mg^{2+}, Fe^{2+} + CO_3^{2-} \rightarrow \text{Ca-Mg-Fe-carbonate}$$

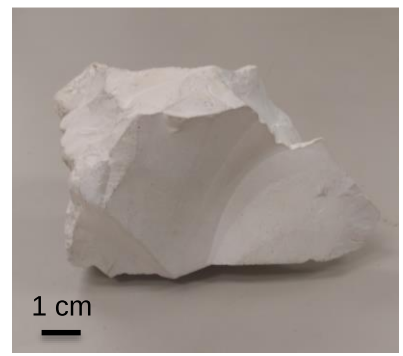
CO_2 promotes silicate dissolution and carbonate precipitation





glass; Ca-Mg-Fe aluminosilicates

calcite, $CaCO_3$



magnesite, $MgCO_3$

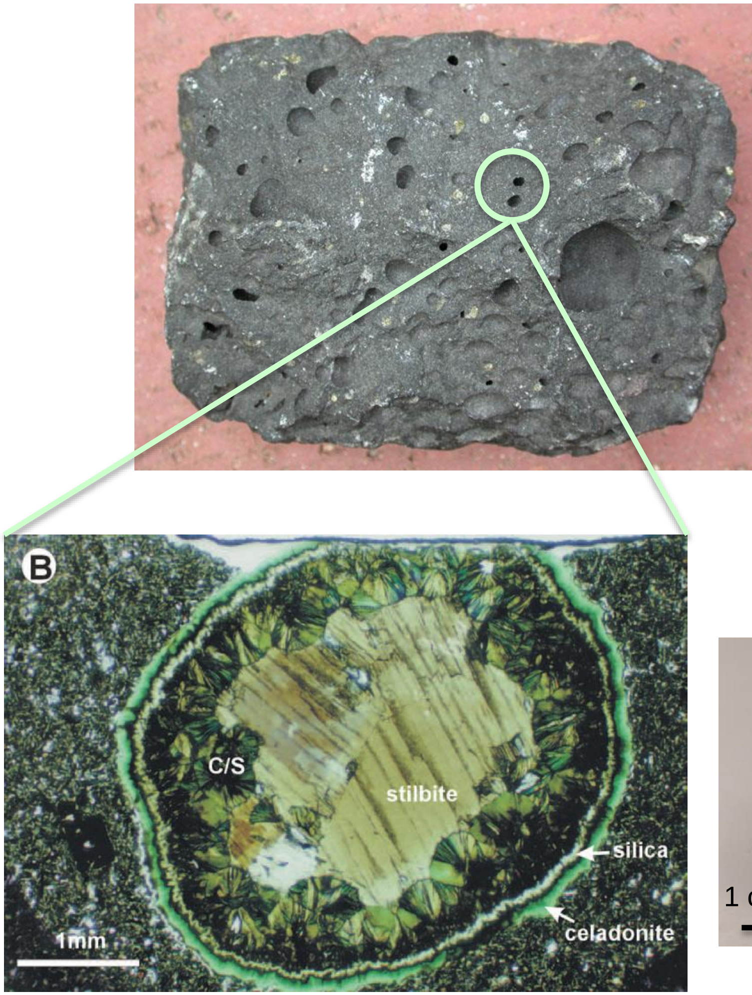
siderite, $FeCO_3$

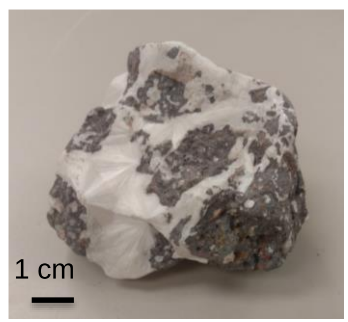
1 mole of plagioclase → 1 mole of CO_2 converted

$$CaAl_2Si_2O_8 + CO_2 + 2H_2O = CaCO_3 + Al_2Si_2O_5(OH)_4$$

~9 tons of basalt → 1 ton of C

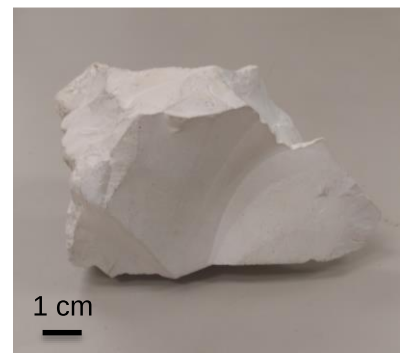
CO_2 promotes silicate dissolution and carbonate precipitation





hydrous secondary Ca-Mg-Fe minerals
(e.g. zeolites)

calcite, $CaCO_3$

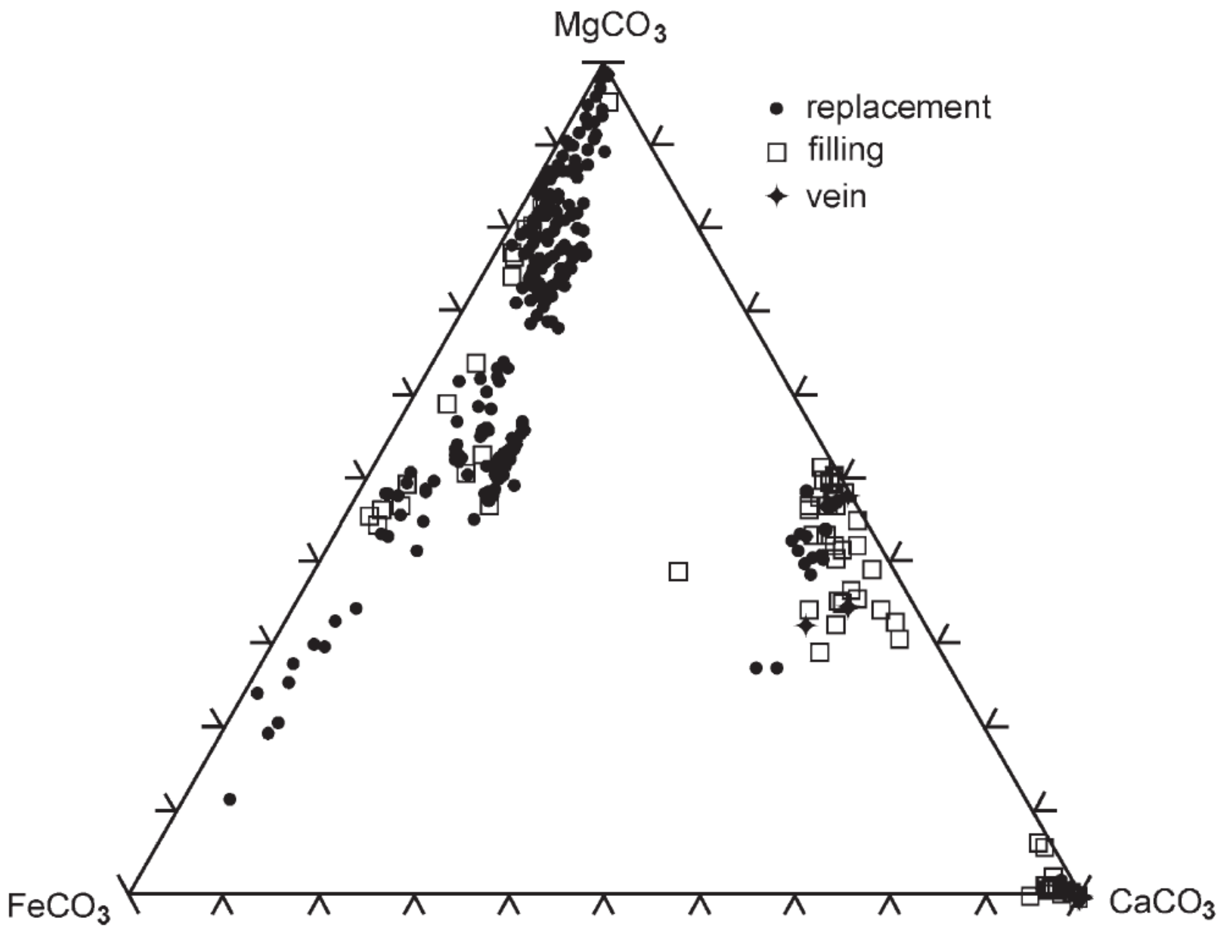


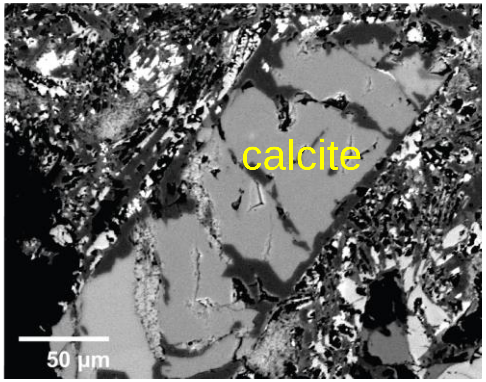
magnesite, $MgCO_3$

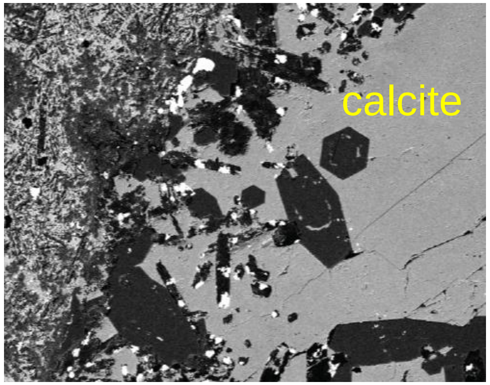
siderite, $FeCO_3$

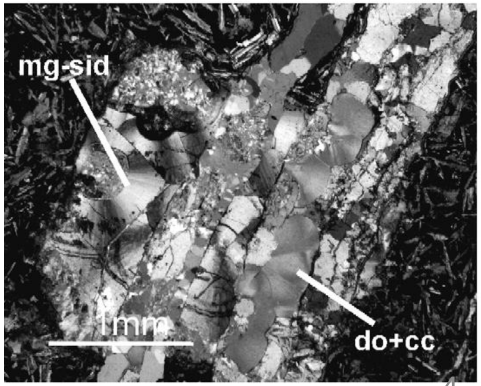
Neuhoff et al. (1999)

Geochemistry and texture of carbonate minerals depends on environment





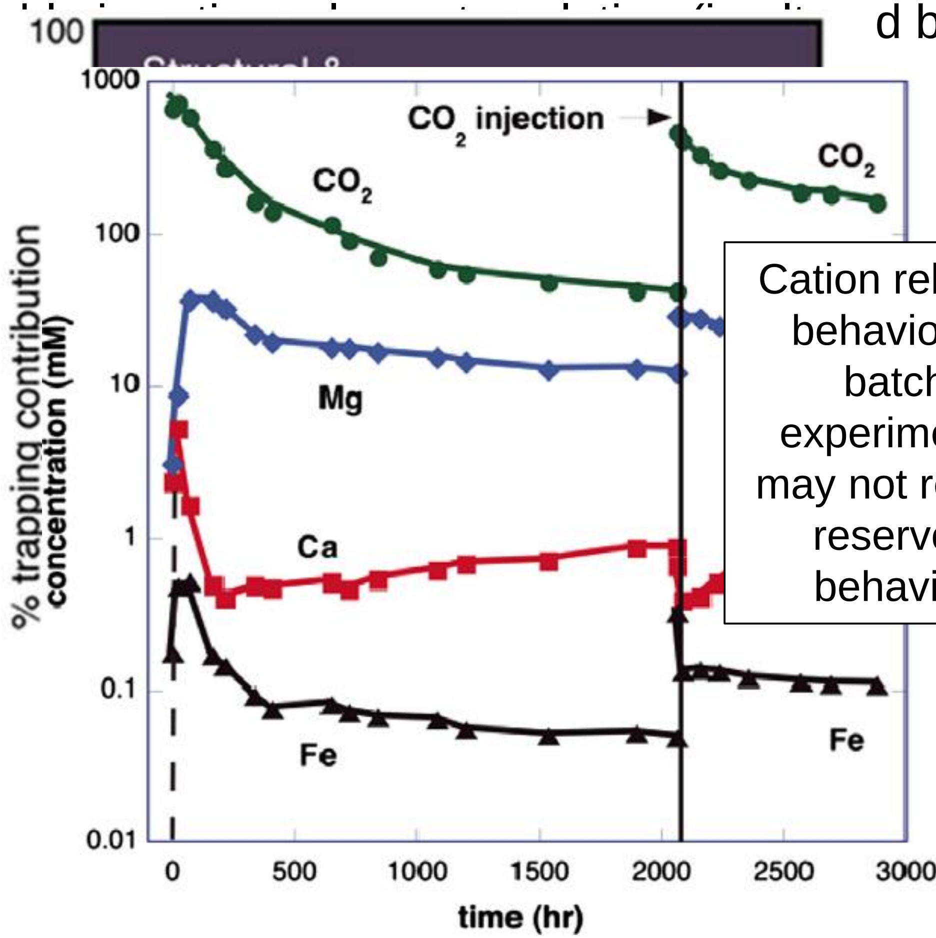




Rogers et al. (2006); Thomas et al. (2016)

Perceived "barriers" to mineral carbonation

1. What is the storage potential? (e.g. compared to sedimentary formations)
2. How fast can CO_2 be transformed?
3. How sustain … d basalt)?

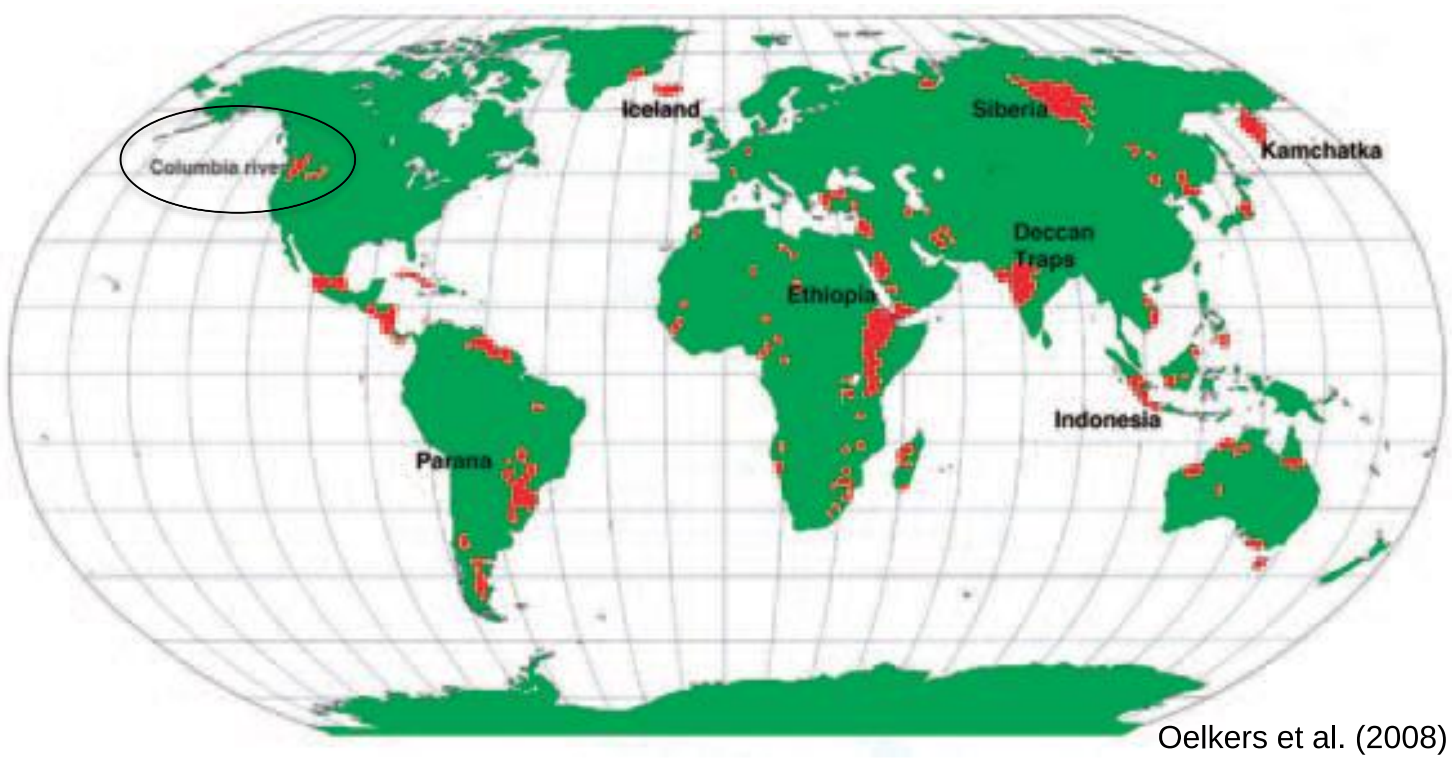


Cation release behavior in batch experiments may not reflect reservoir behavior

Benson et al. (2005) (IPCC)
Rosenbauer et al. (2012)

Storage capacity is potentially enormous.

Basalts cover ~5% of the continents and most of the ocean floor.



Oelkers et al. (2008)

Columbia River flood basalts
>100 Gt CO_2

Juan de Fuca Plate (offshore)
~900 Gt CO_2

Snæbjörnsdóttir and Gislason, 2016

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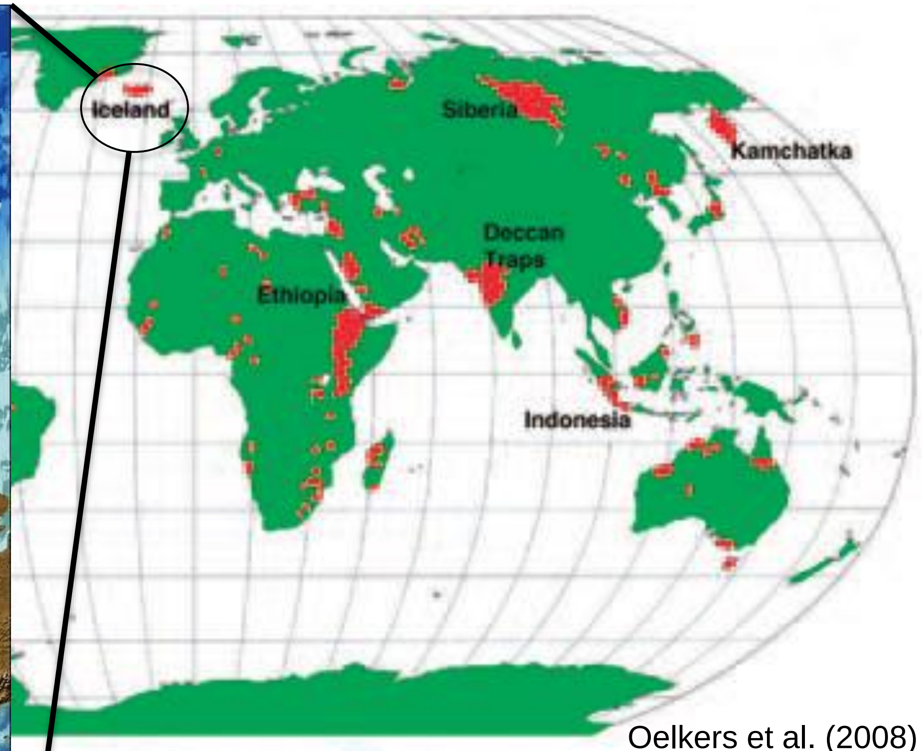
Snæbjörnsdóttir and Gislason, 2016

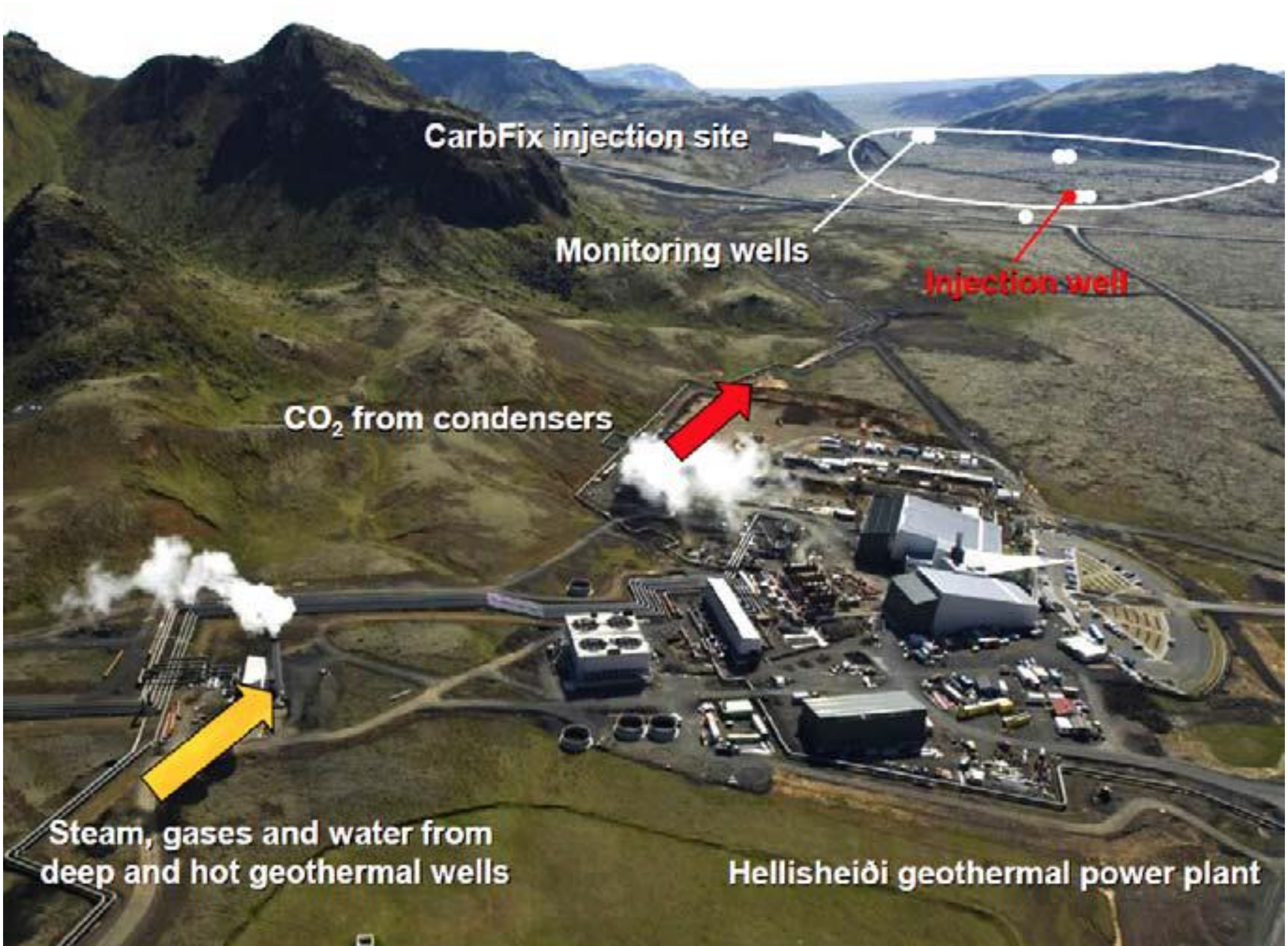


Oelkers et al. (2008)

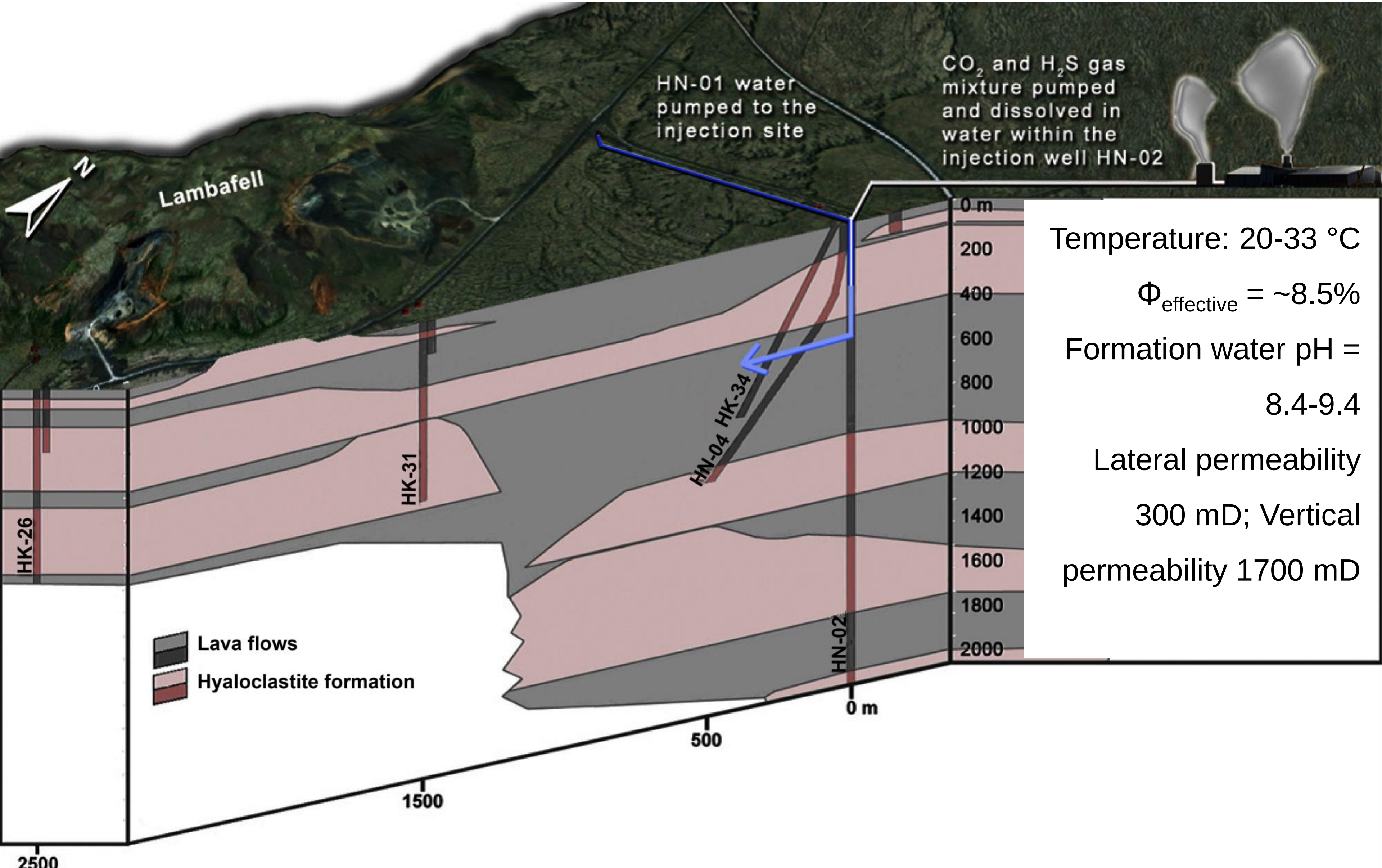
Iceland

Onshore: 400-2,000 Gt CO_2
Offshore: 7,000 Gt CO_2

Field validation of mineral carbonation: the CarbFix project



Field validation of mineral carbonation: the CarbFix project



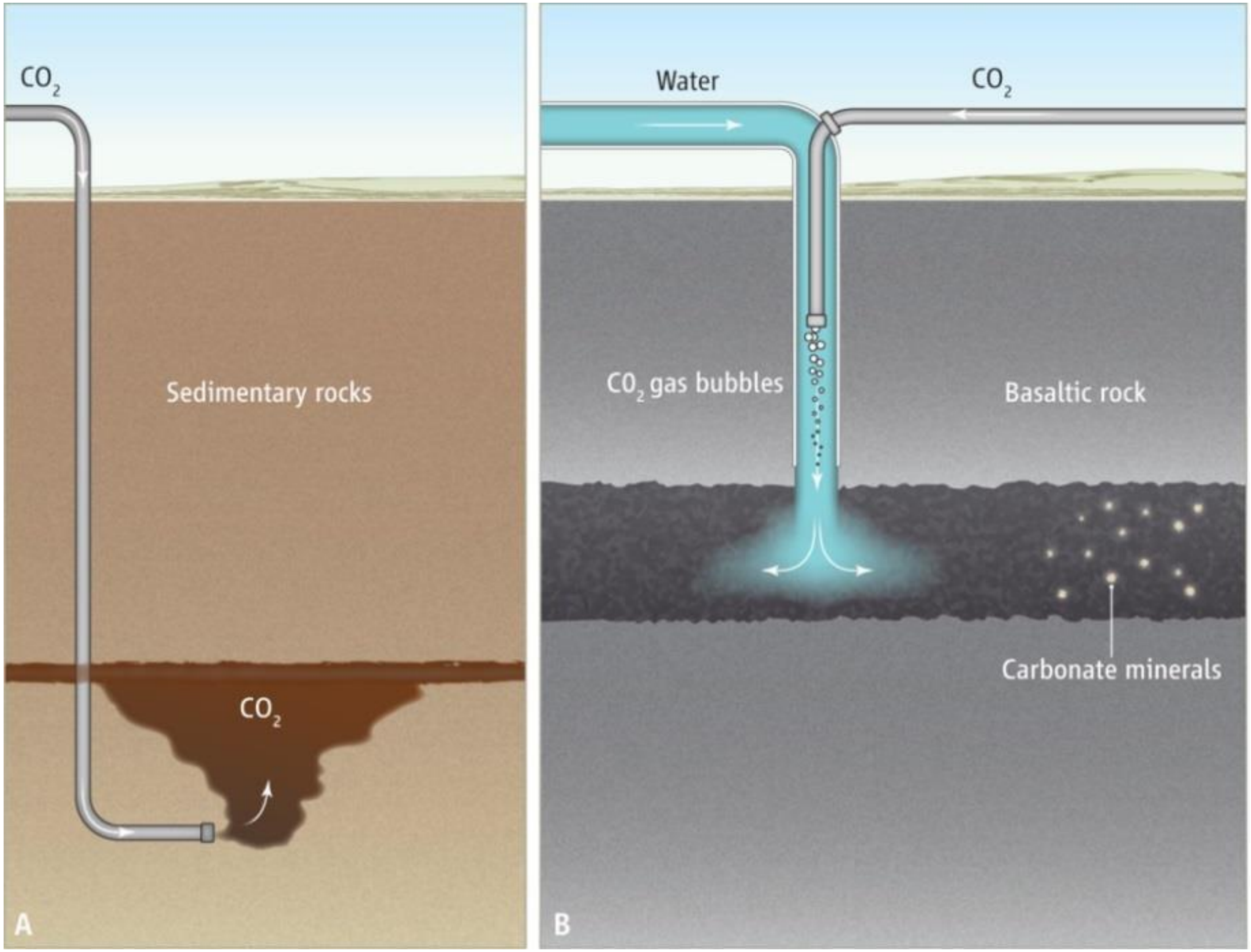
Temperature: 20-33 °C

$\Phi_{effective}$ = ~8.5%

Formation water pH = 8.4-9.4

Lateral permeability 300 mD; Vertical permeability 1700 mD

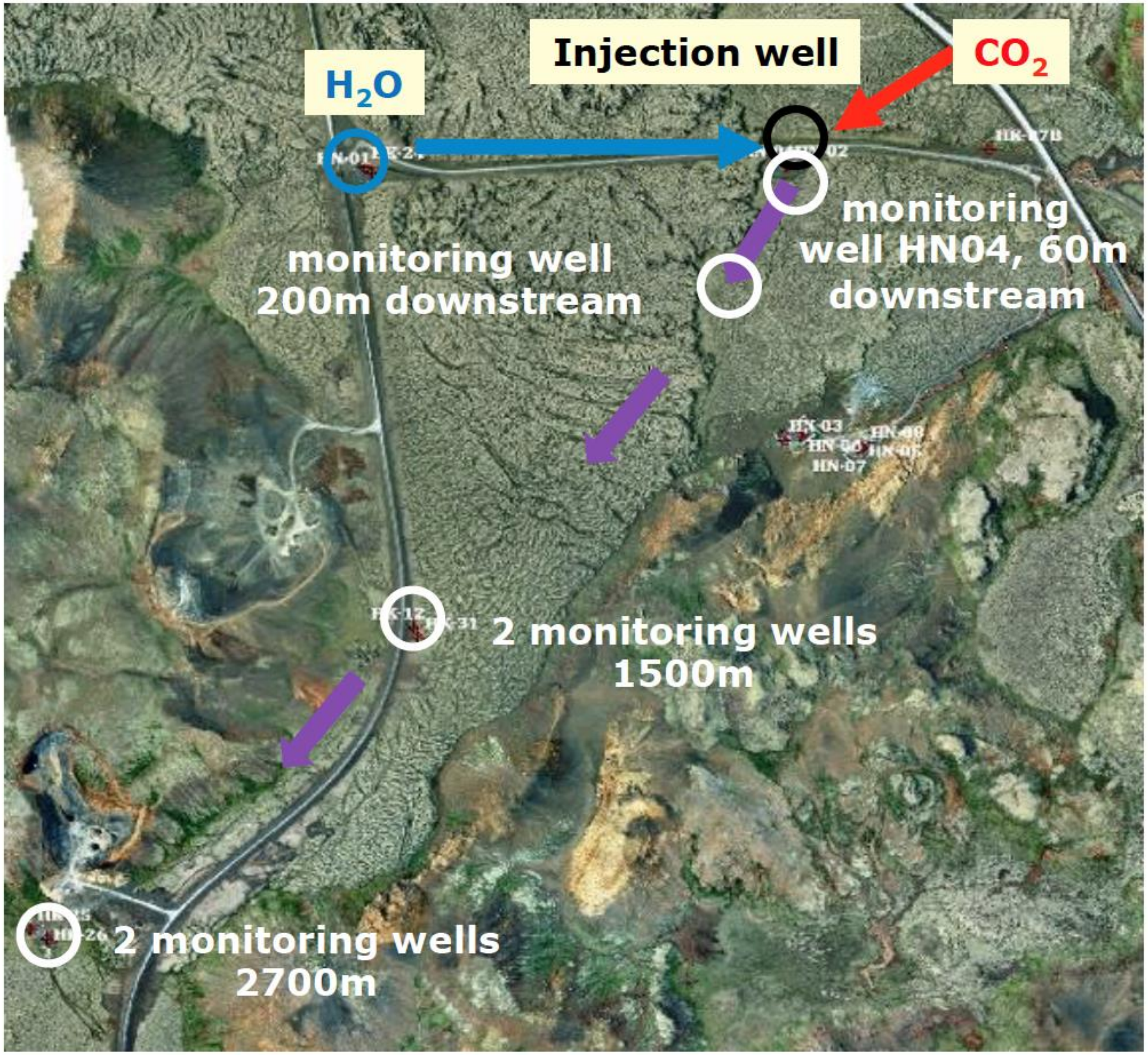
Field validation of mineral carbonation: the CarbFix project



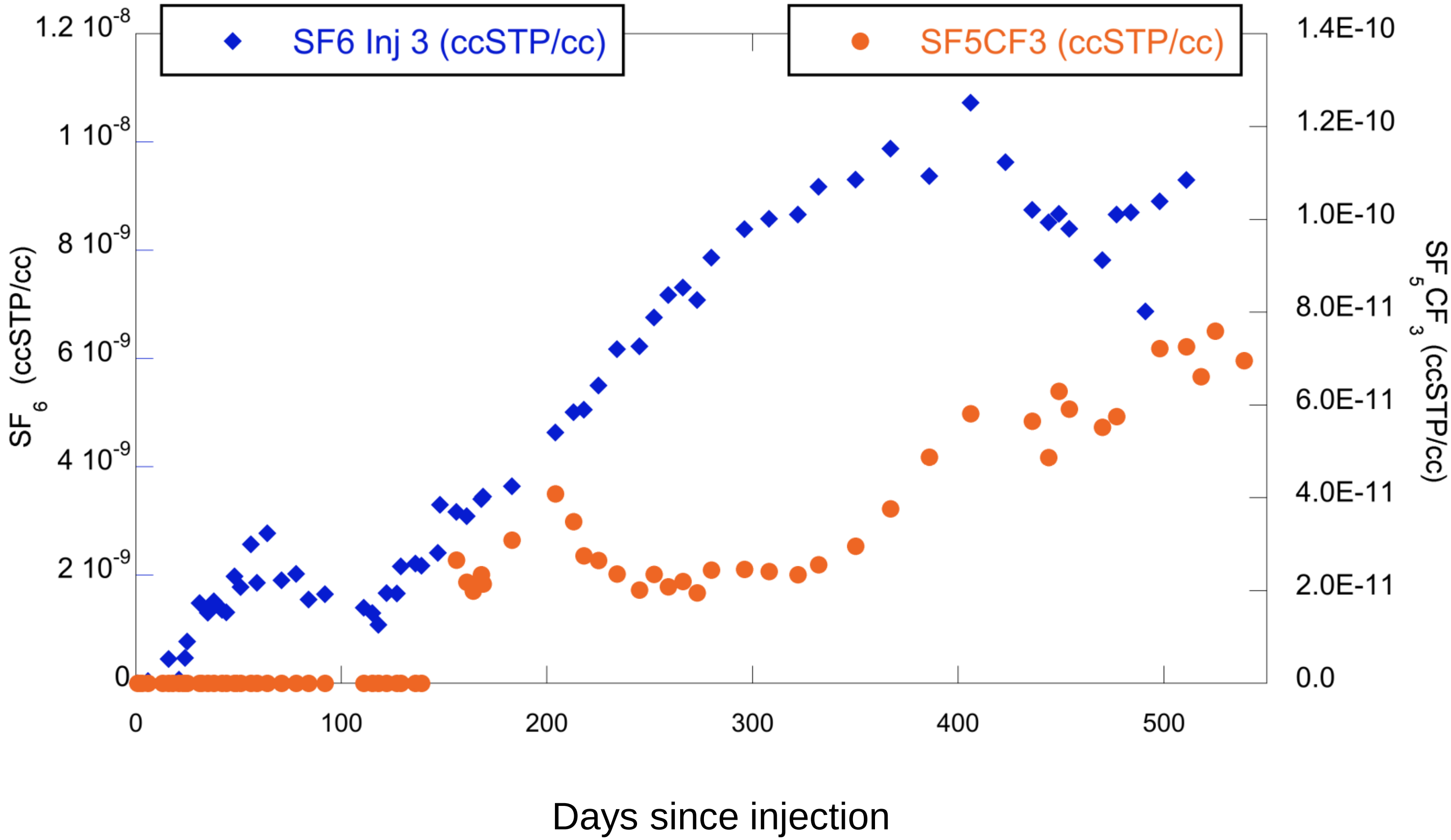
175 tons of CO_2 injected January – March 2012

73 tons of CO_2+H_2S injected June 2012

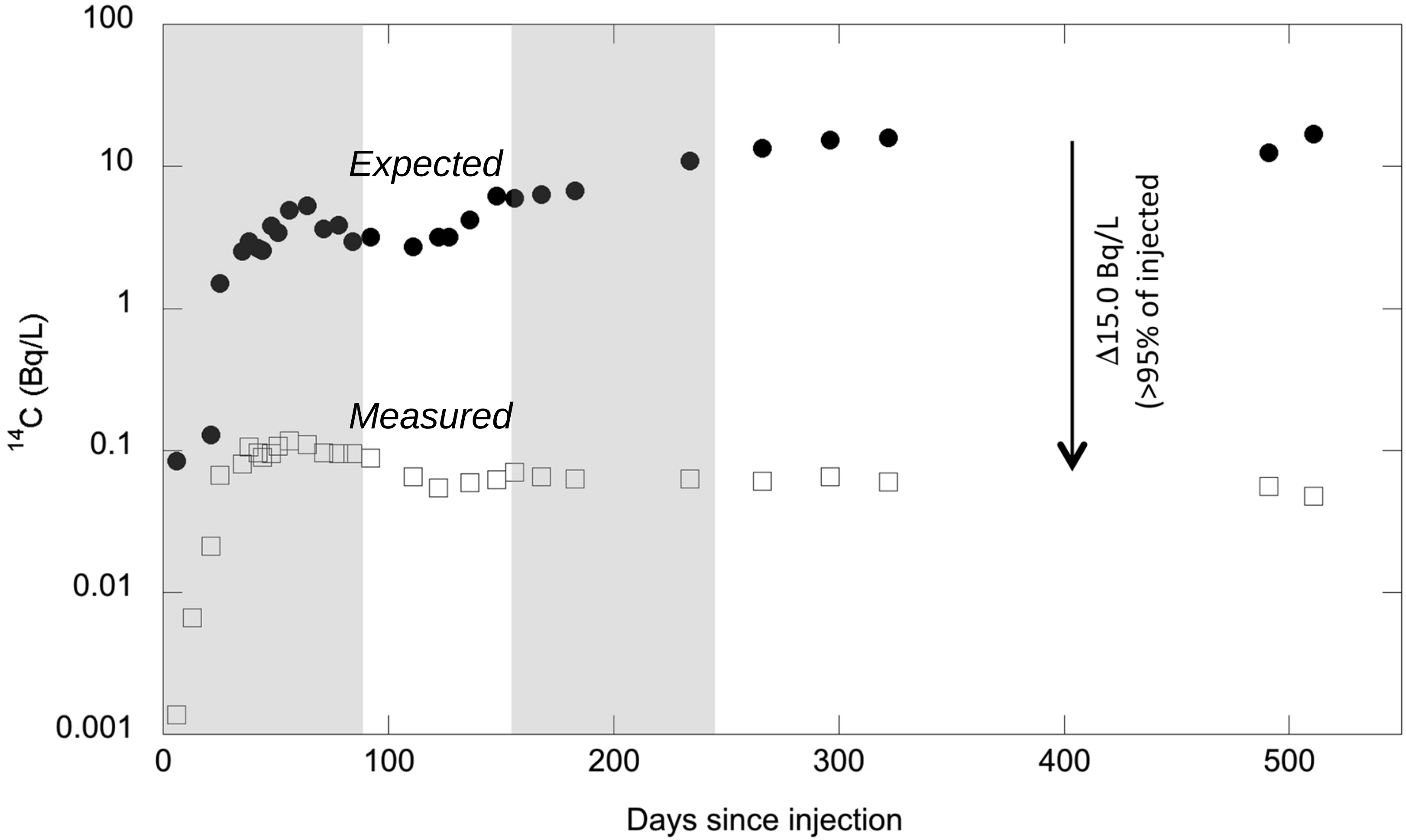
Field validation of mineral carbonation: the CarbFix project



Monitoring shows recovery of injected tracers



>90% of injected CO_2 assumed converted to carbonate minerals



Where did mineralization occur?

Geochemical and physical parameters must be known to make quantitative predictions

Reactants

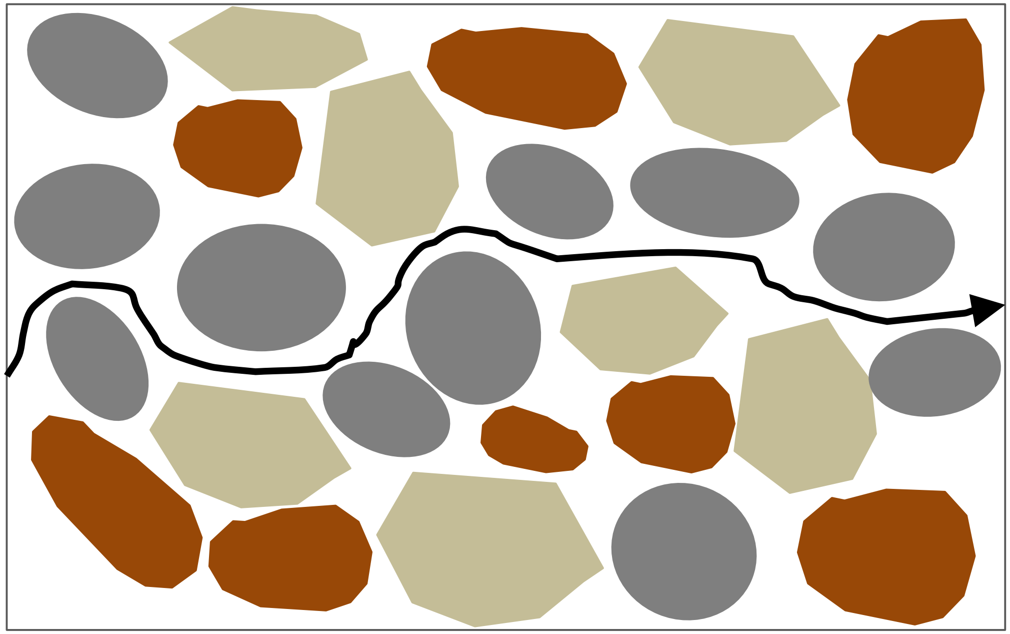
Reactive Surface Area

Flow path geometry

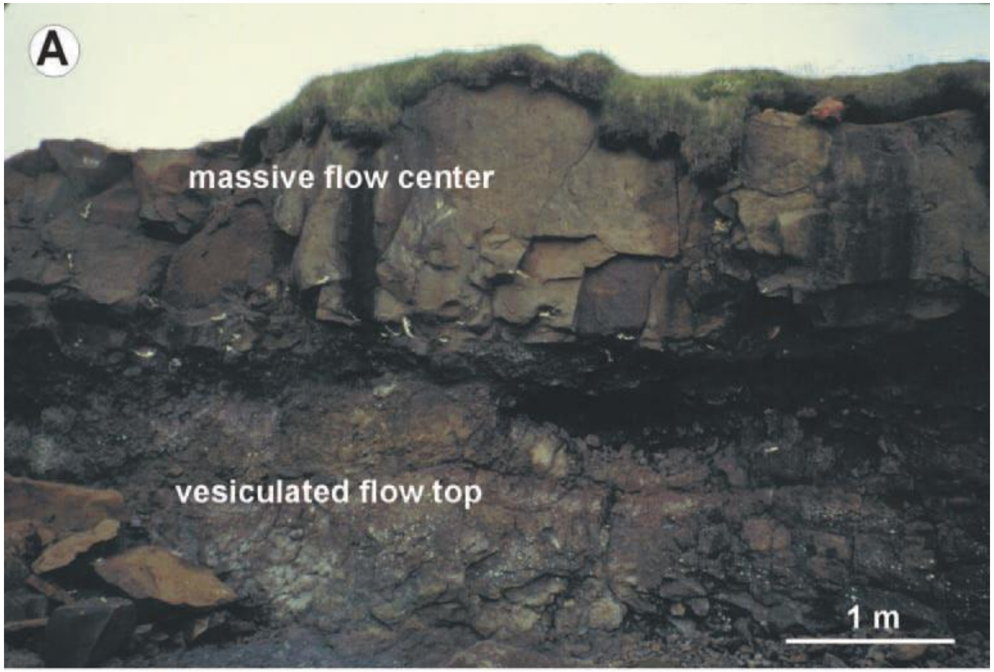
Porosity

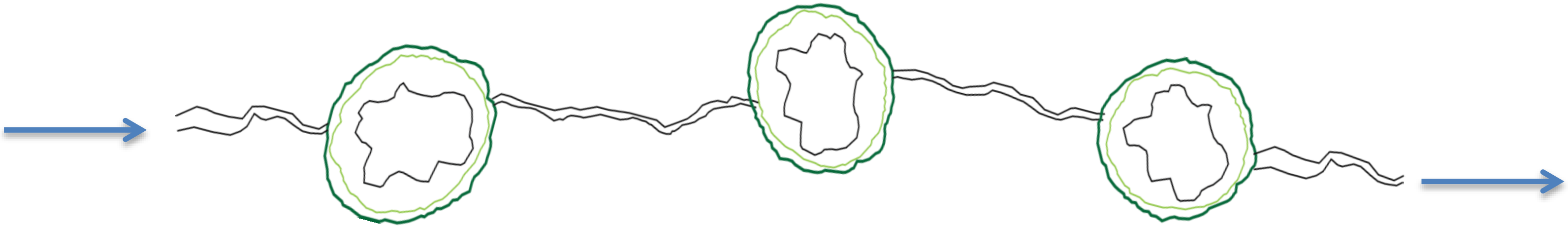
Permeability

Dissolution Rate



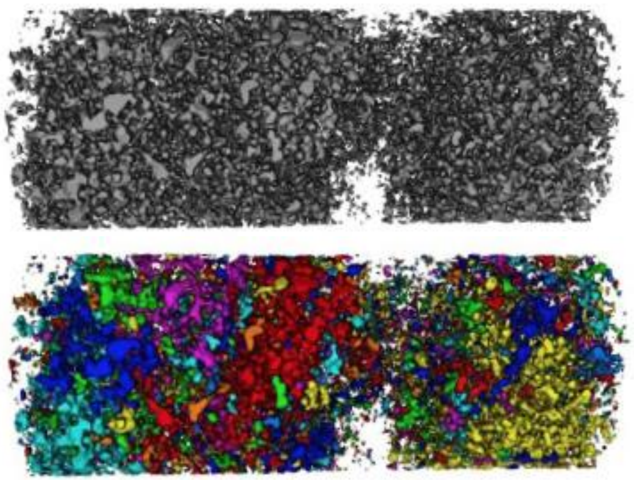
How does the extent and rate of reaction depend on flow path and mineral distributions?

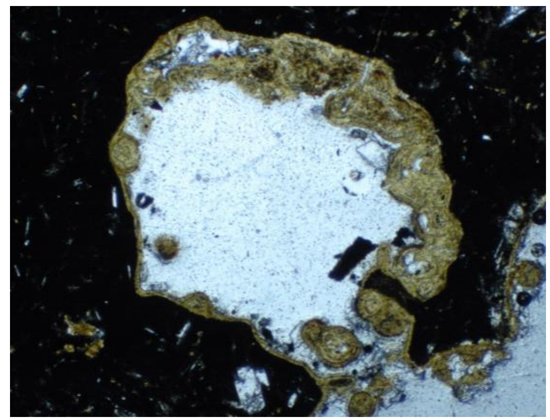


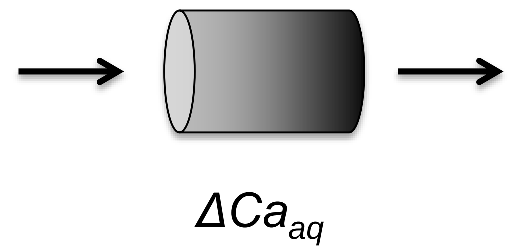


Reactants, Flow path geometry & Reactive Surface Area

How does the extent and rate of reaction depend on flow path and mineral distributions?







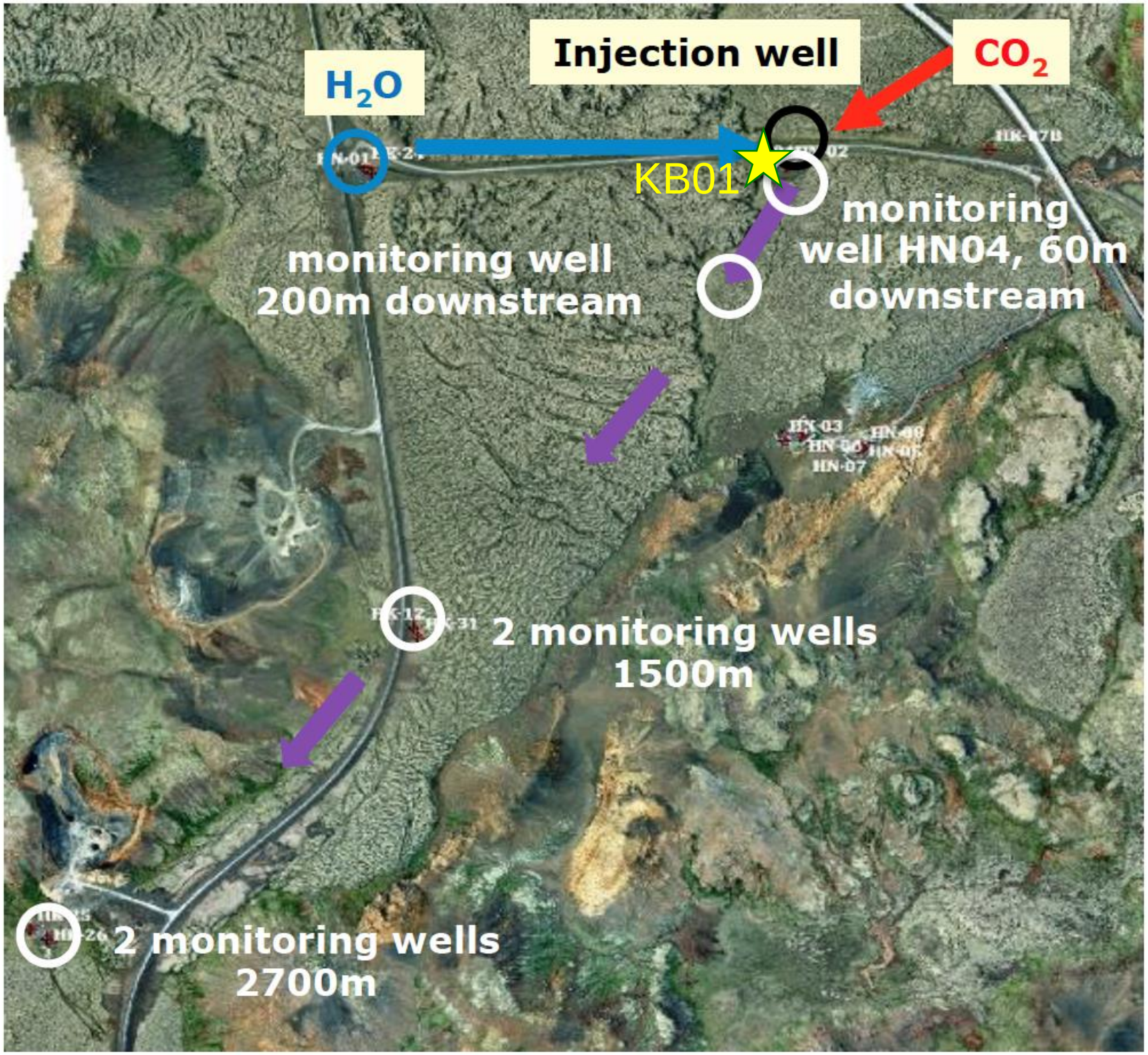
imaging + petrography + geochemistry

medical CT
micro CT
PET scanning

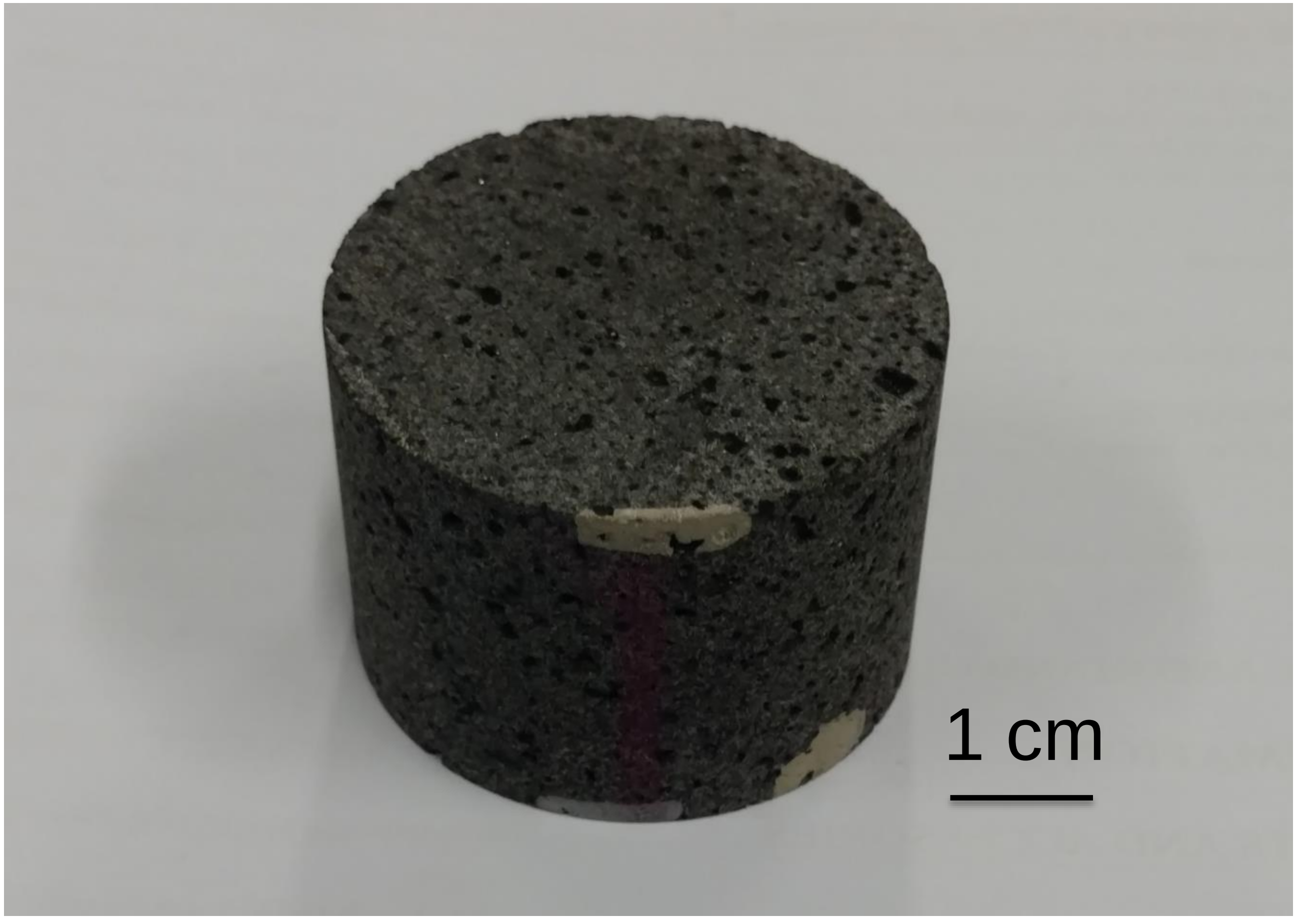
mineralogy

aqueous solute release
thermodynamic analysis
dissolution kinetics

Basaltic core from CarbFix site for experiment

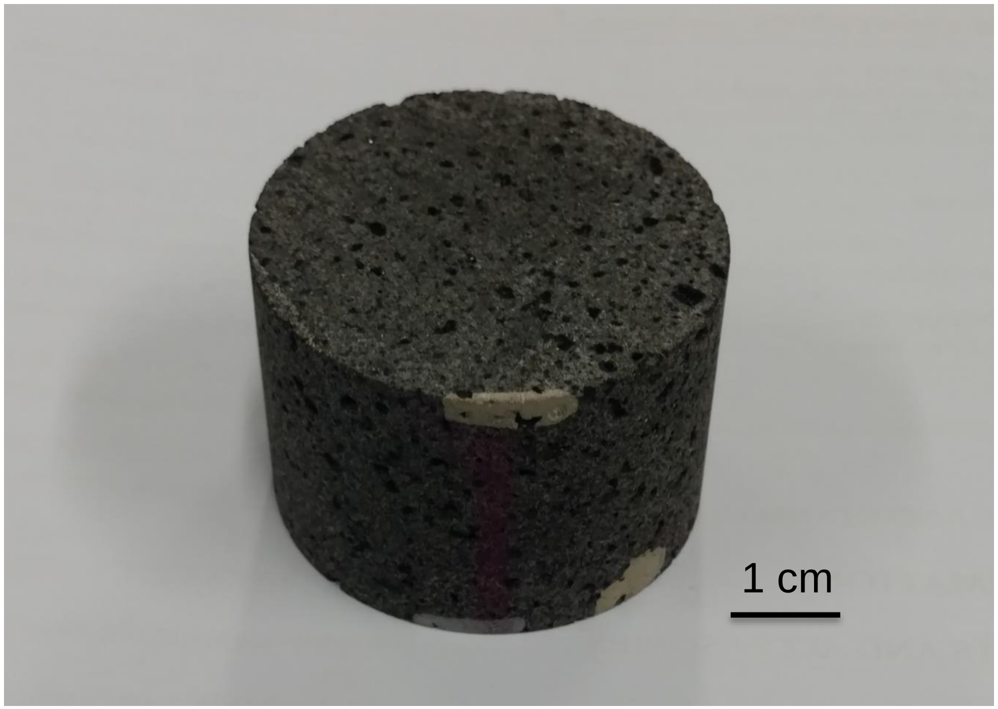


Core KB01-6-4



- 4.5 cm diameter, 3.5 cm length
- from 400 m below surface
- $k = 4\ \mu D\ (4 \times 10^{-18}\ m^2)$; $\Phi_{total} = 11\%$

Experimental observations of basalt-CO_2 interaction

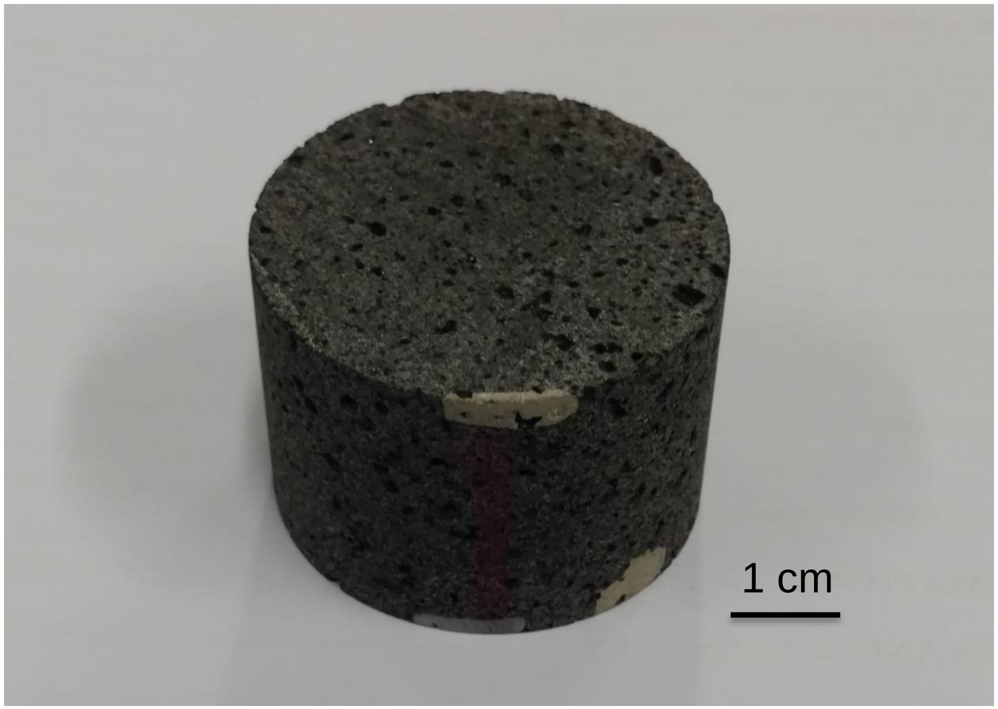


1. Image flow paths and pore structure (PET and microCT)

2. Reactive flow-through experiment

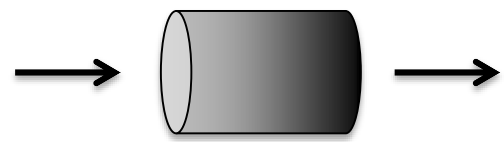
3. Post-reaction imaging

Experimental observations of basalt-CO_2 interaction

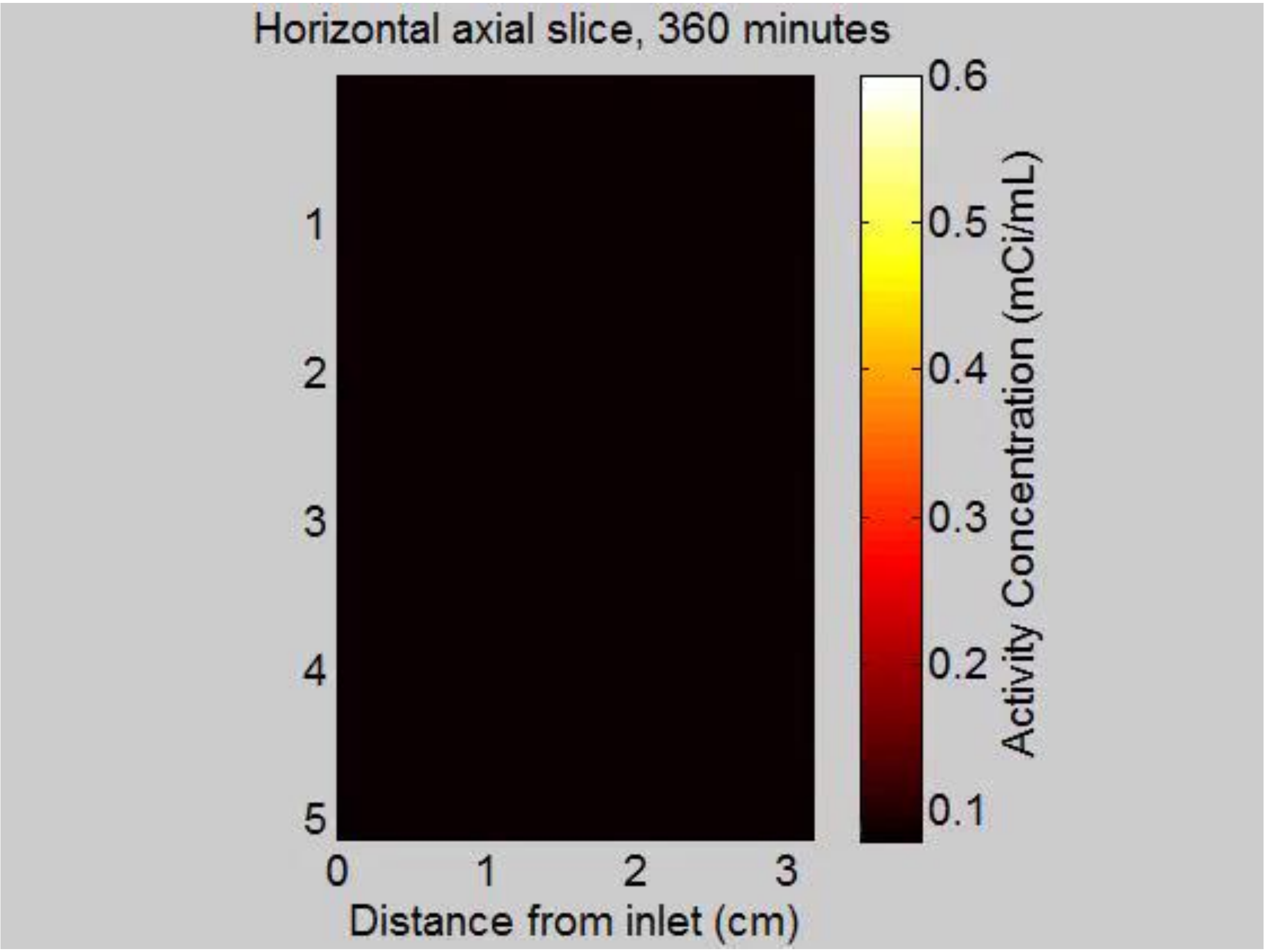


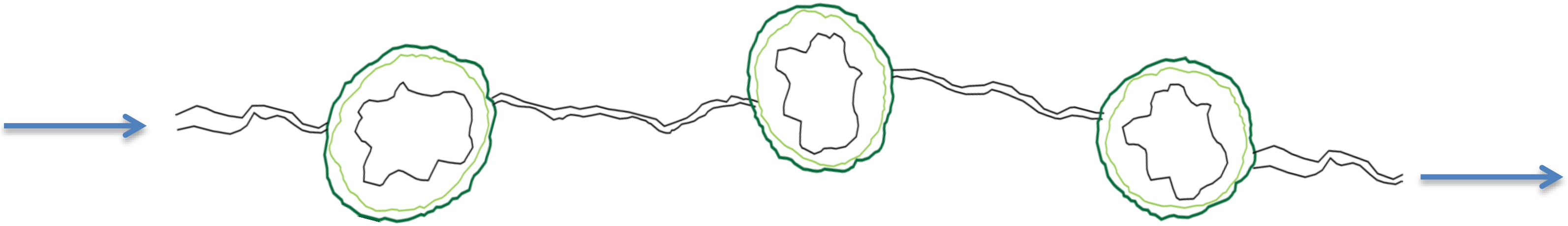
1. Image flow paths and pore structure (PET and microCT)

pulse of radioactive tracer (F18)

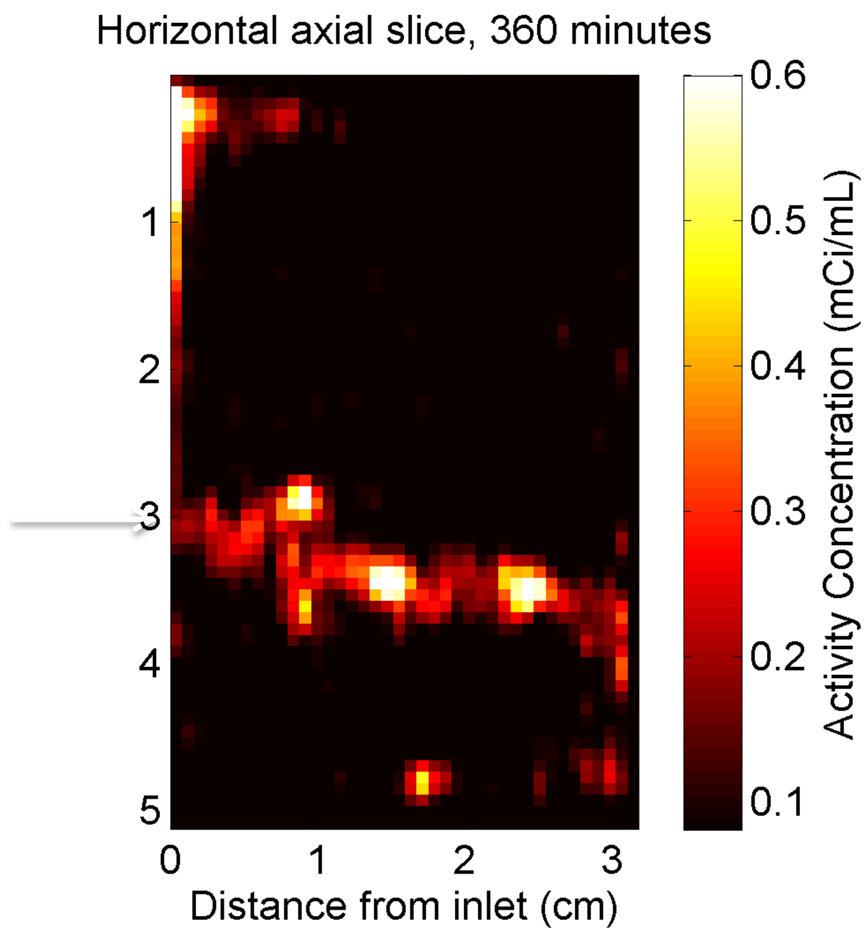


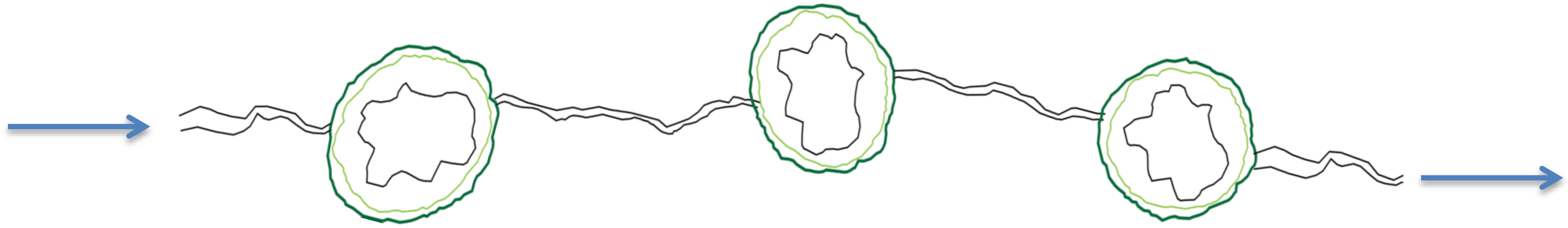
Flow is localized along a single channel connecting vesicles



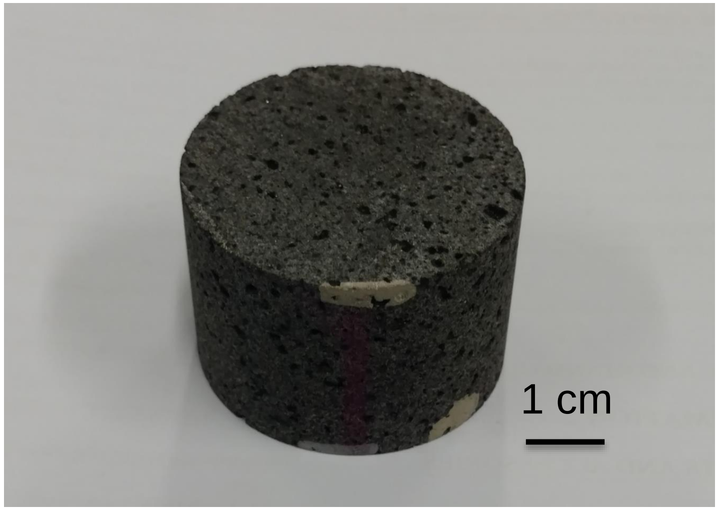


Flow is localized along a single channel connecting vesicles



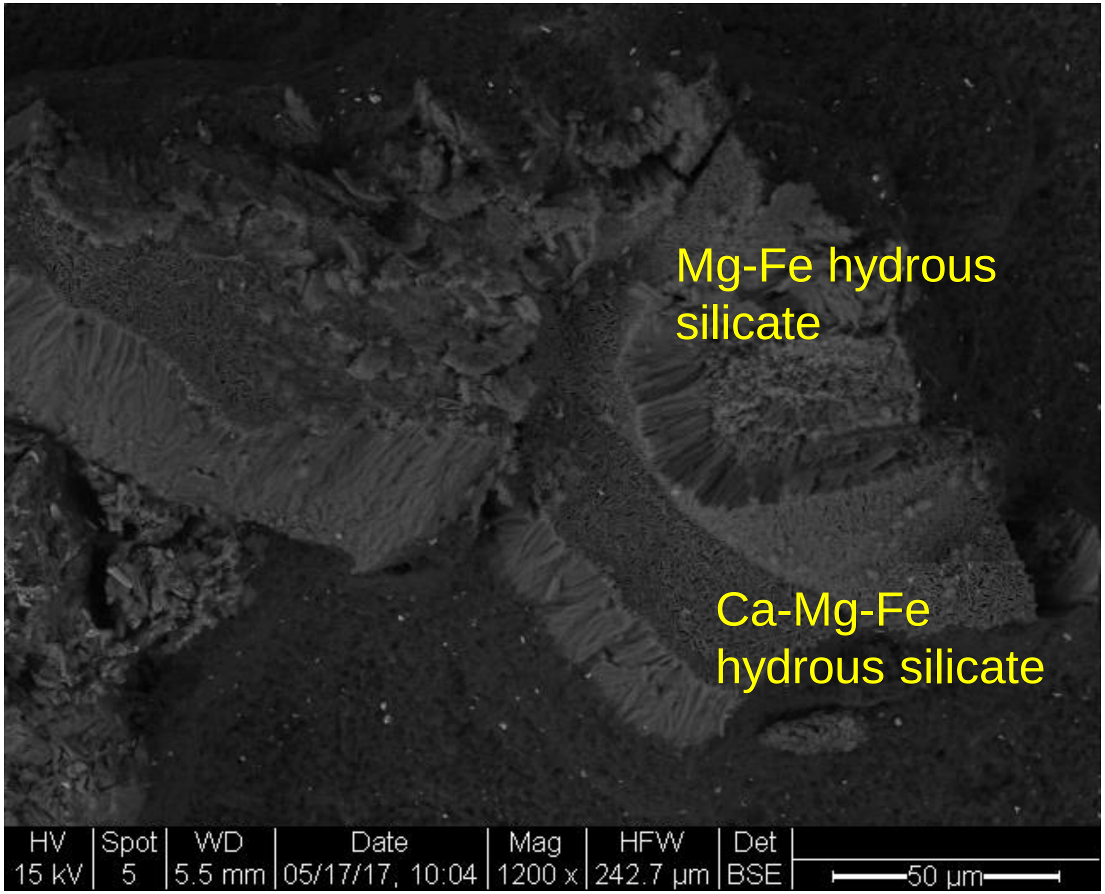


Reactive phases are present in matrix and lining vesicles

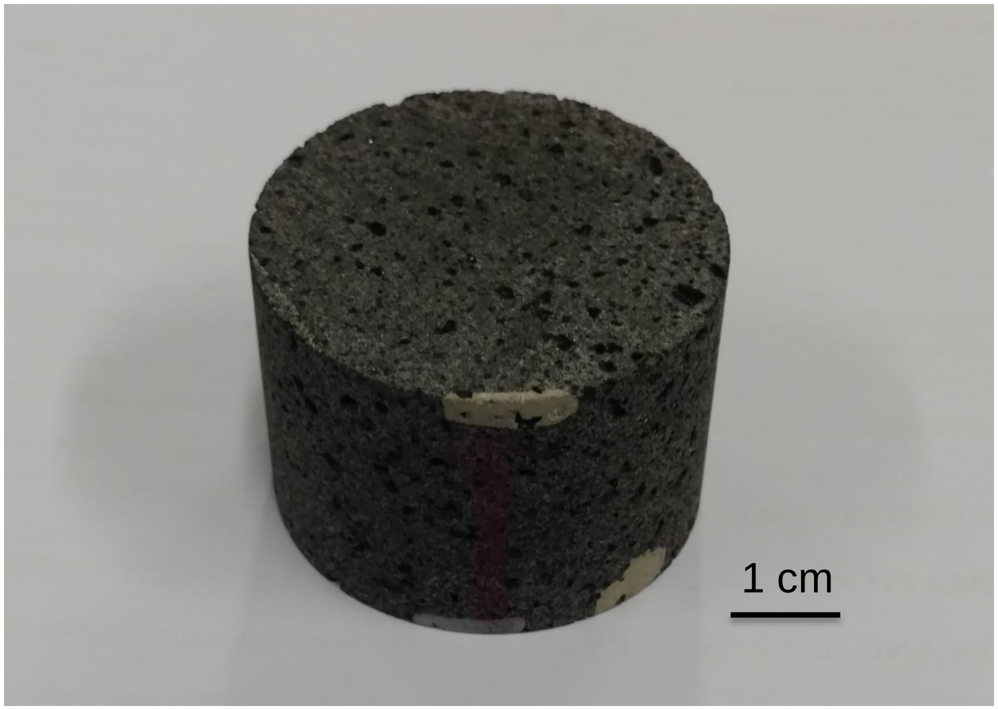


Matrix:
Glass (Na-K-Mg-Fe-Ca)
Plagioclase feldspar
Ca-Mg-Fe pyroxene

Vesicles:
(Ca-) Mg-Fe phyllosilicates
Ca-zeolite



Experimental observations of basalt-CO_2 interaction



2. Reactive flow-through experiment

50 °C

0.1 mol/kg NaCl

P_{CO2} = 1100 psi

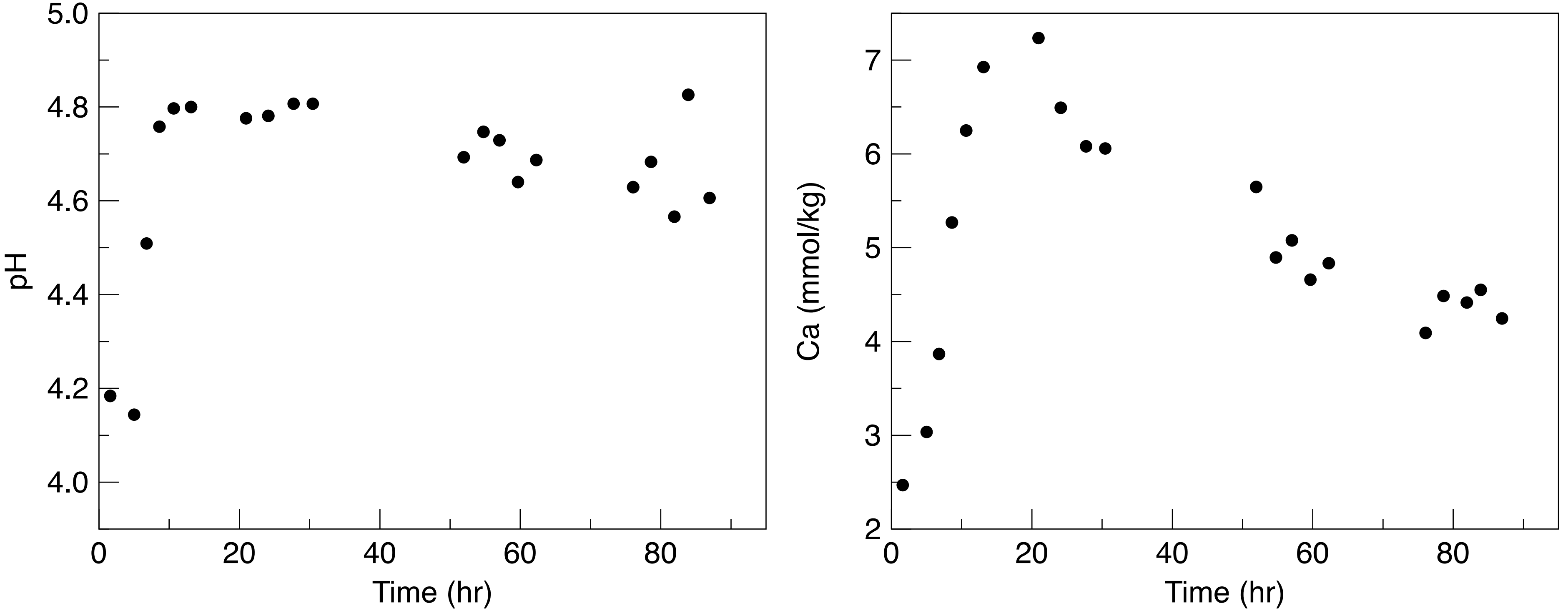
CO_2 (aq) = 0.985 mol/kg

pH = 3.2

Q = 0.015 mL/min

ΔCa_{aq}

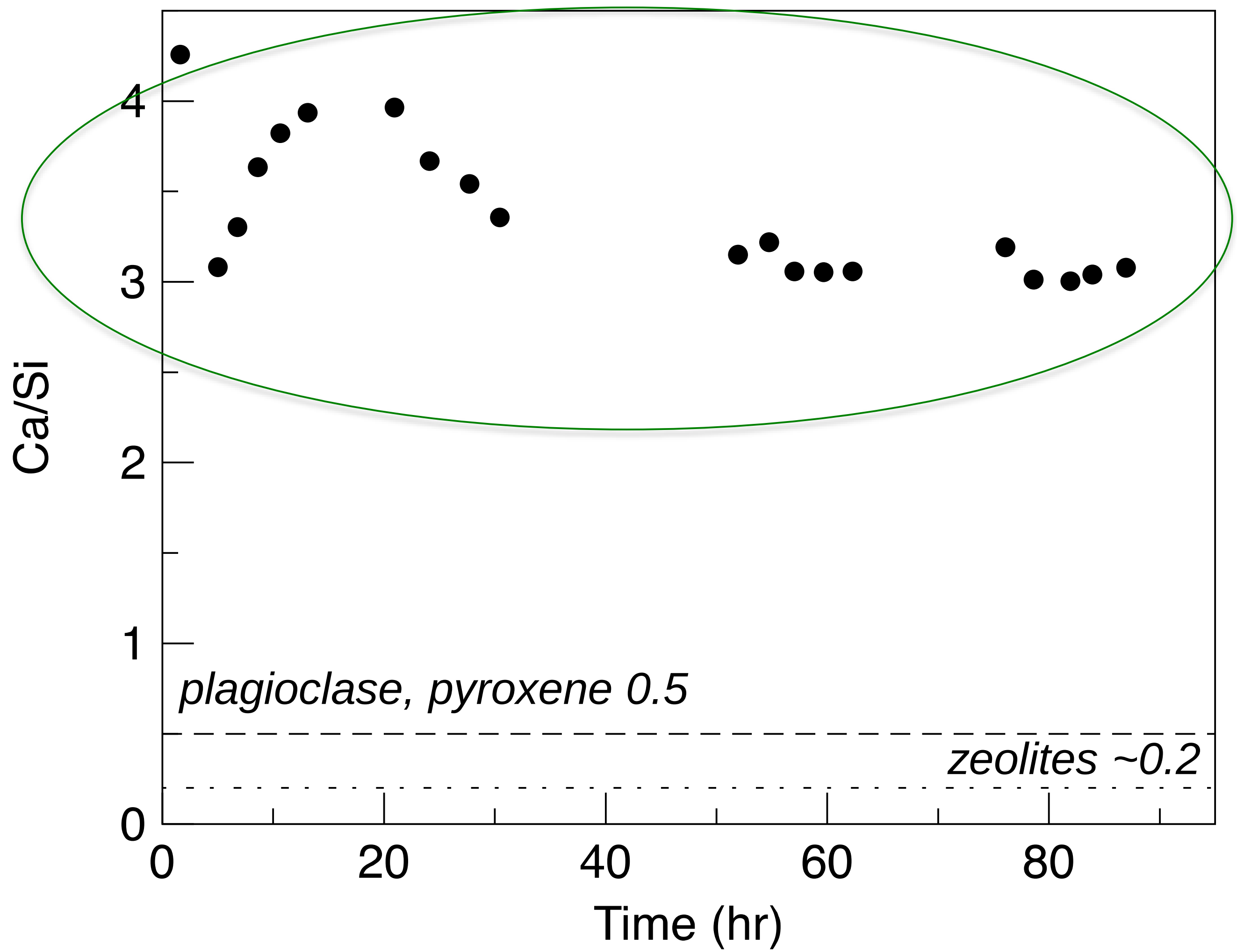
Aqueous results imply immediate and rapid dissolution



$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-$

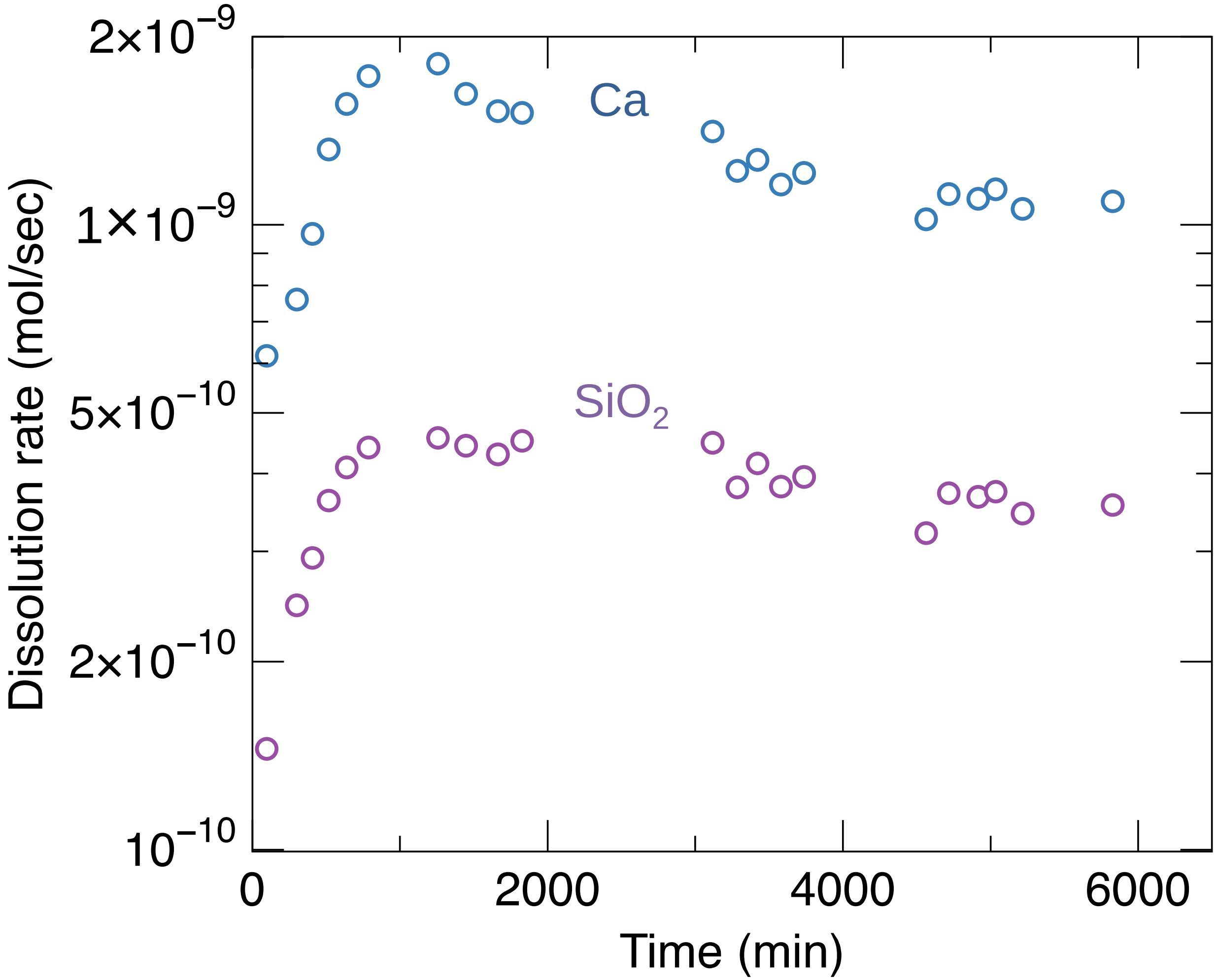
$\text{Ca-silicate} + H^+ \rightarrow Ca^{2+} + SiO_2\,(aq)$

High cation: silica ratios imply cation leaching and/or ion exchange



Ca-mineral + Na^+ (aq) → Ca^{2+} (aq) + Na-mineral

“Dissolution rate” slows with time



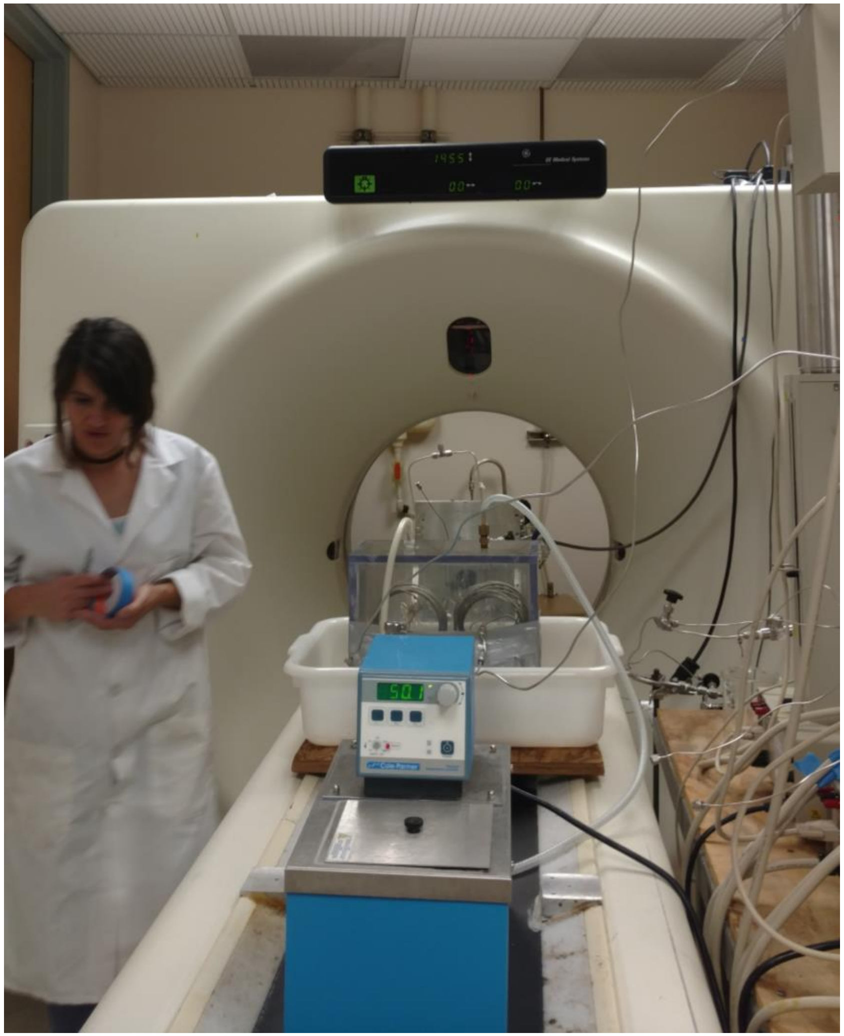
Experimental observations of basalt-CO_2 interaction: recycled flow to promote approach to equilibrium

4.5 cm diameter, 11.2 cm length = 178.13 cm^3

Porosity (from medical CT) = 25%; Permeability (from flow test): 1.2 mD

Pore volume = 44.5 cm^3

Experimental observations of basalt-CO_2 interaction: recycled flow to promote approach to equilibrium



Flow-through experiment

26 days

50 °C

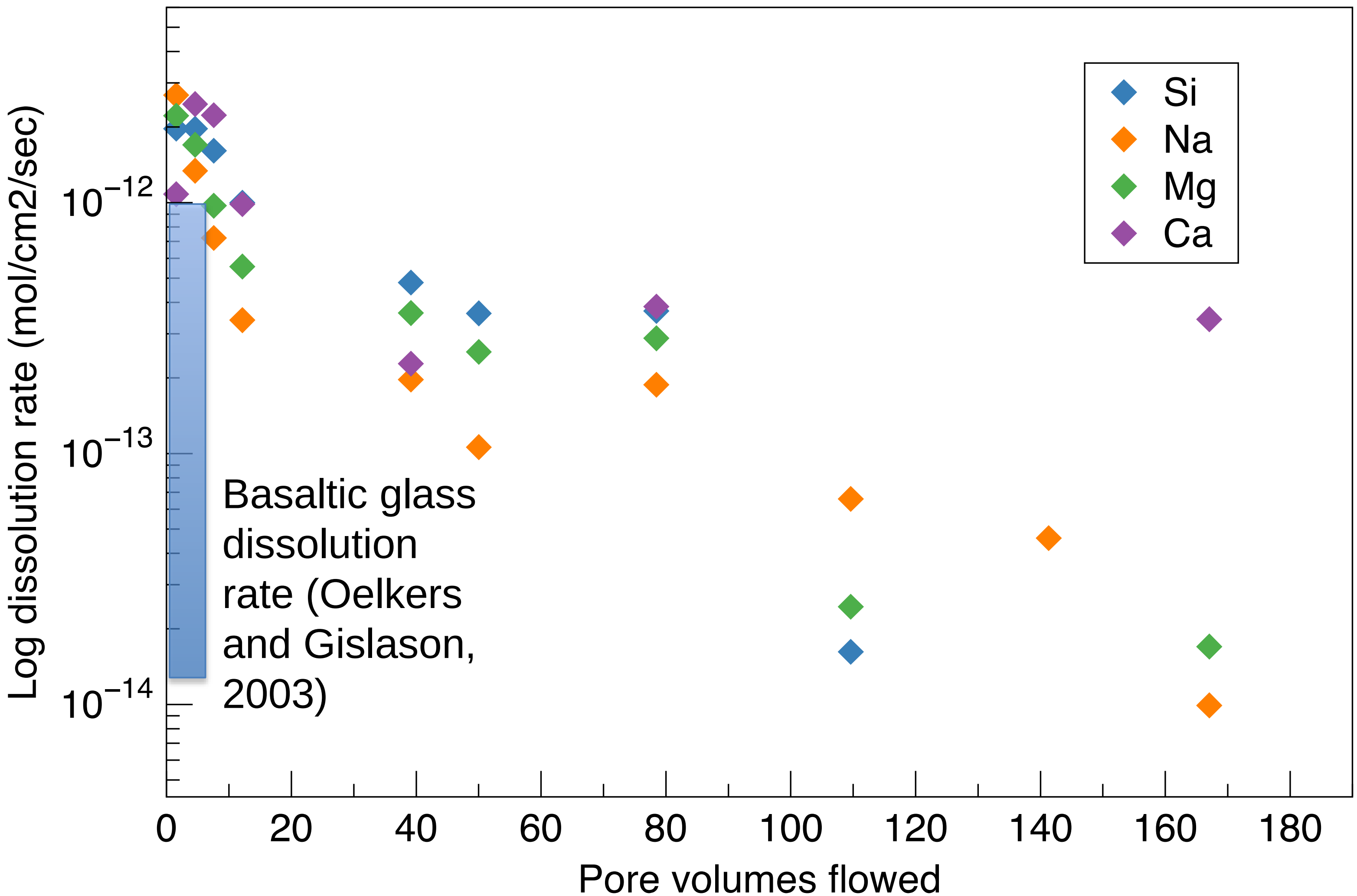
P_{CO2} = 90 bar

1.07 mol/kg CO_2 (aq)

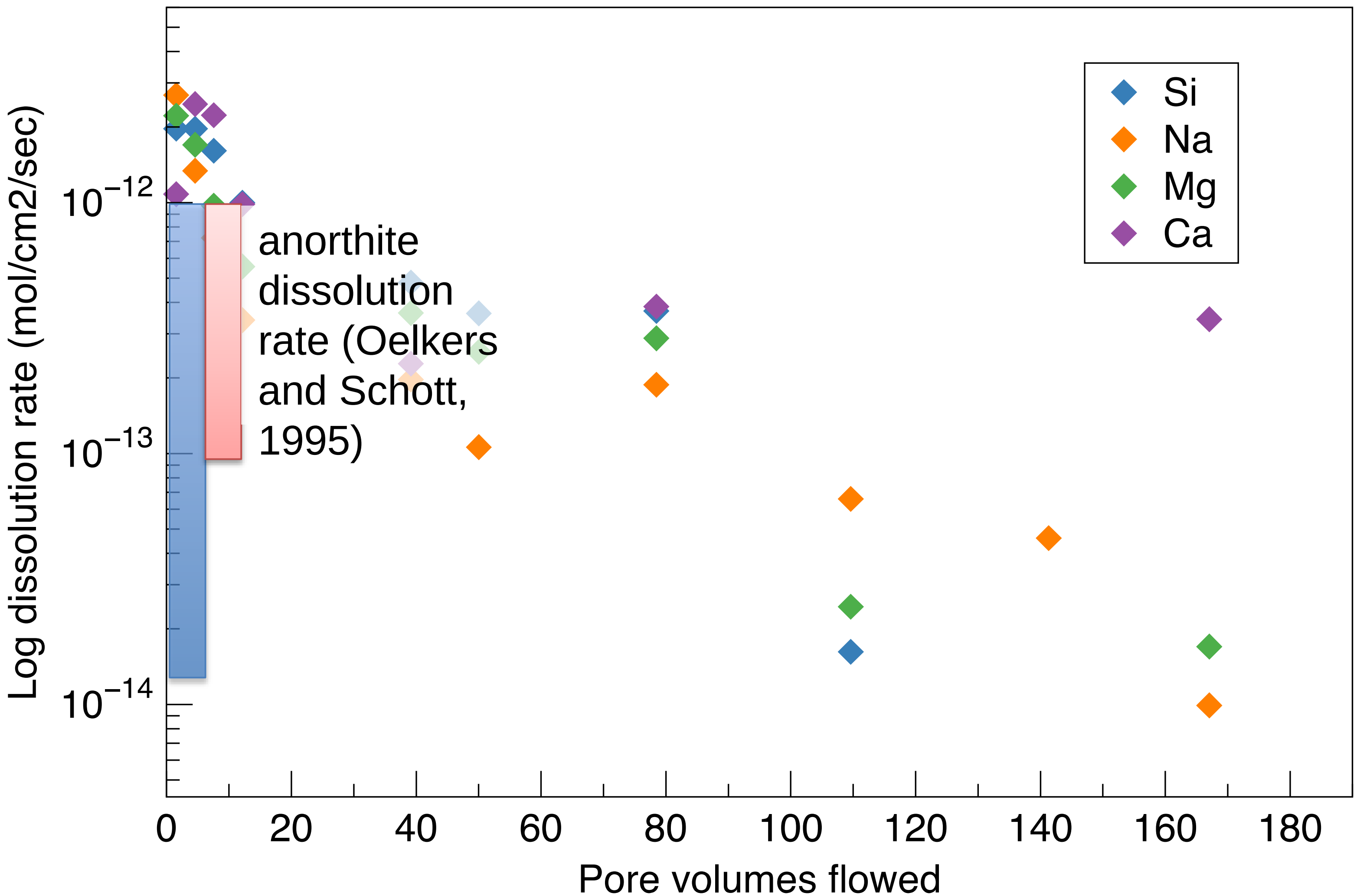
pH (calculated) = 3.3

Q = 0.2 mL/min

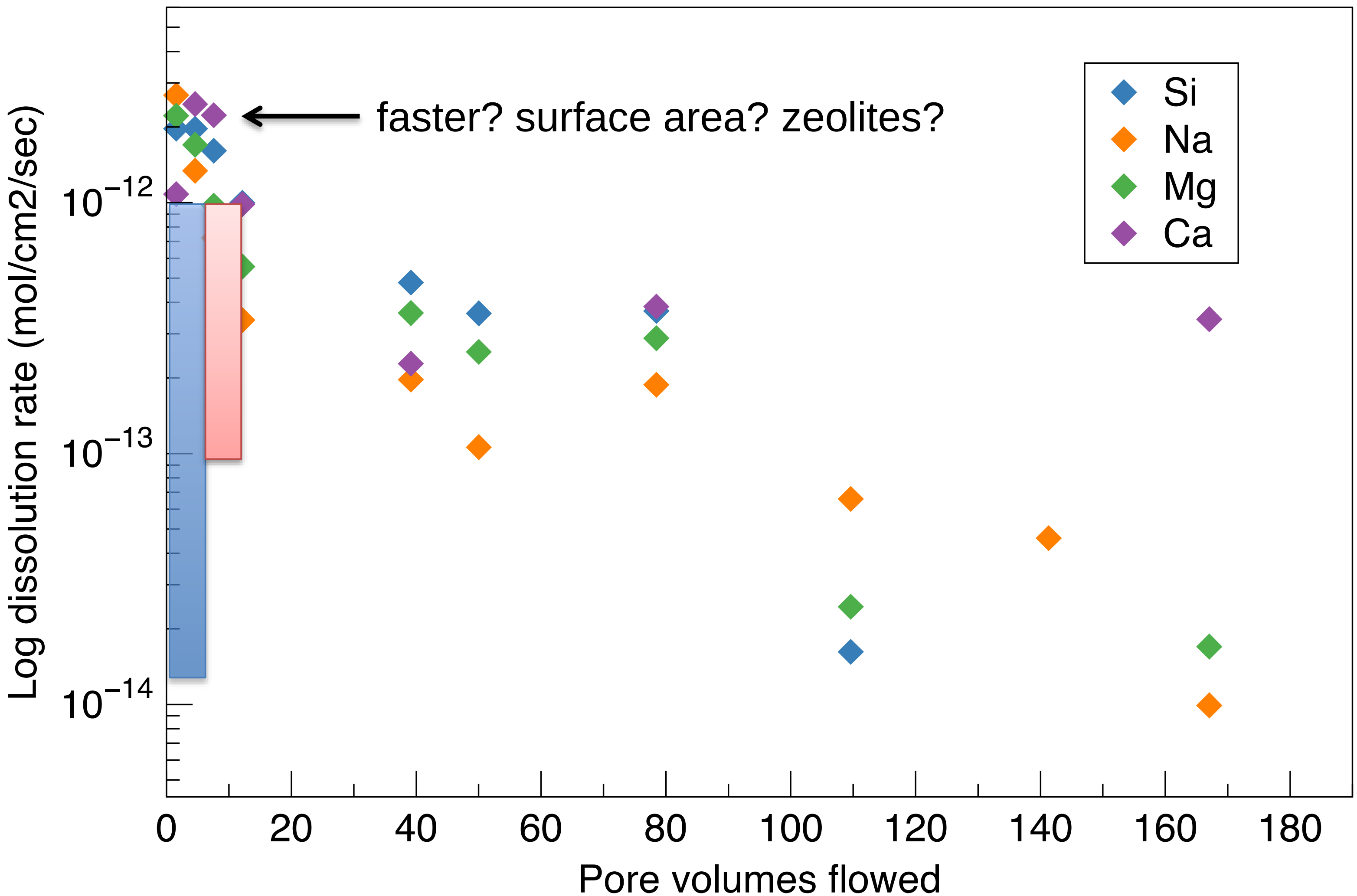
“Surface area normalized dissolution rate” [mol/cm²/sec]



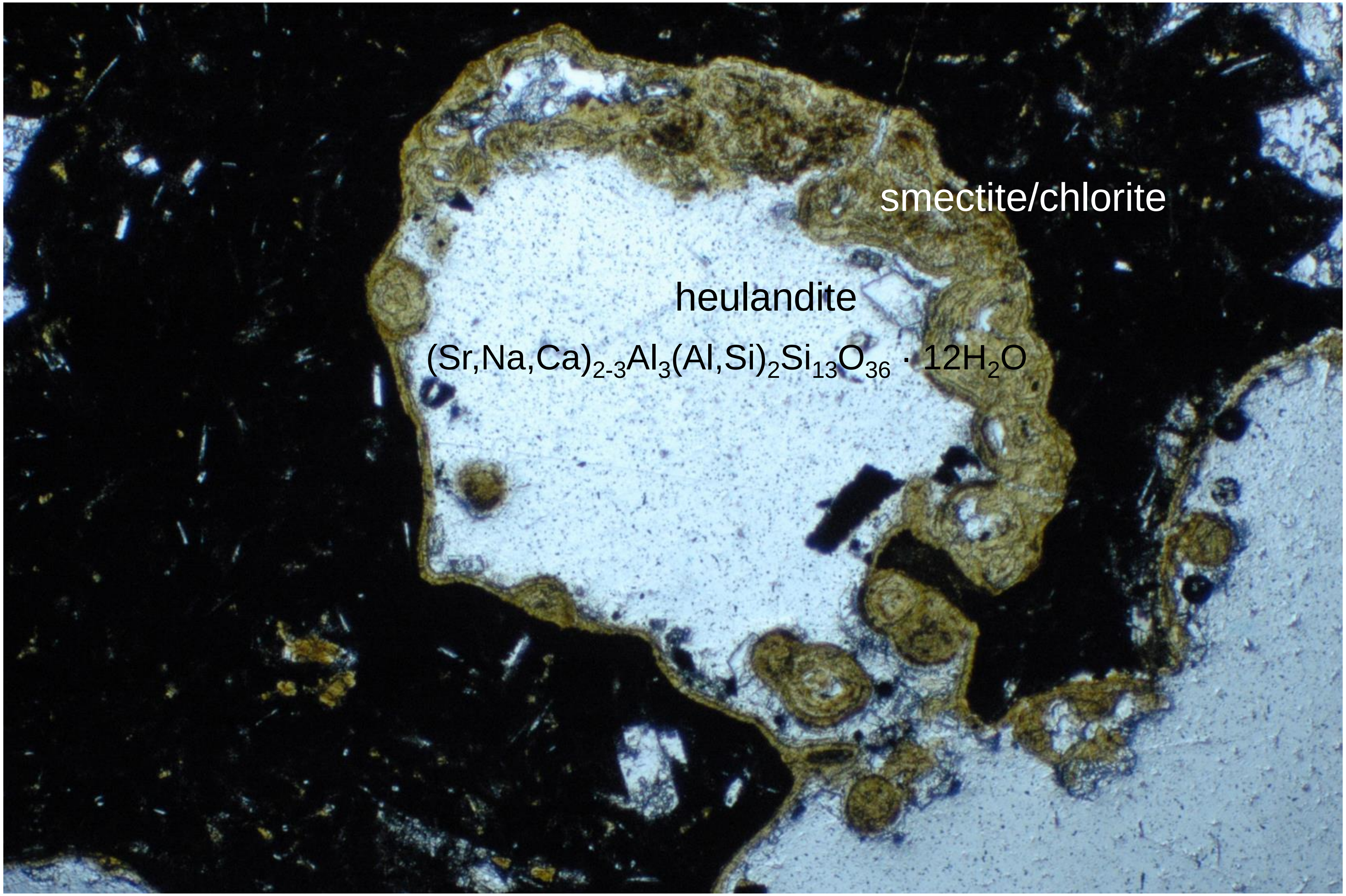
“Surface area normalized dissolution rate” [mol/cm²/sec]



“Surface area normalized dissolution rate” [mol/cm²/sec]

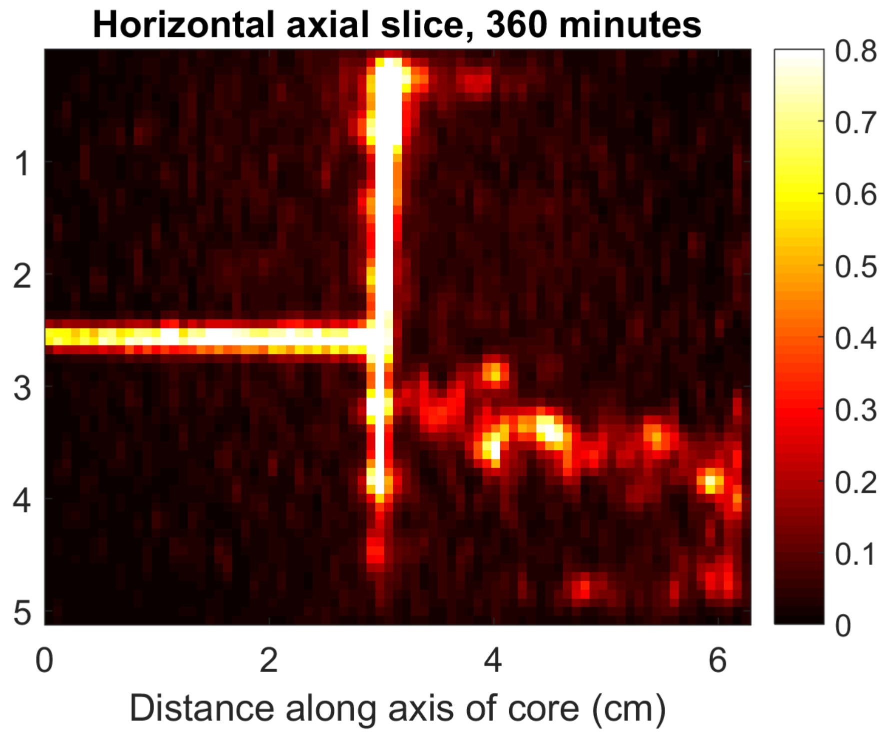


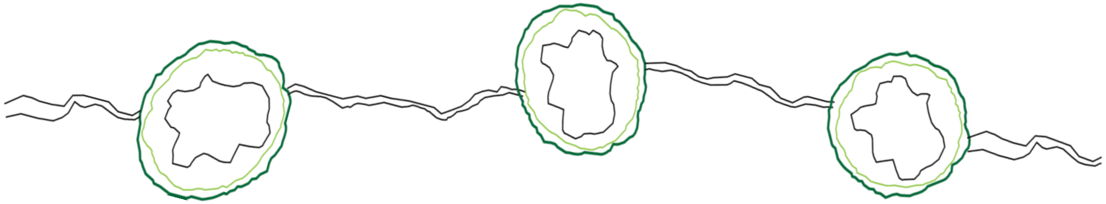
First-to-react phases yield initial spike in divalent cations



FOV: 1.78 mm
(vesicle is ~0.85 mm across)

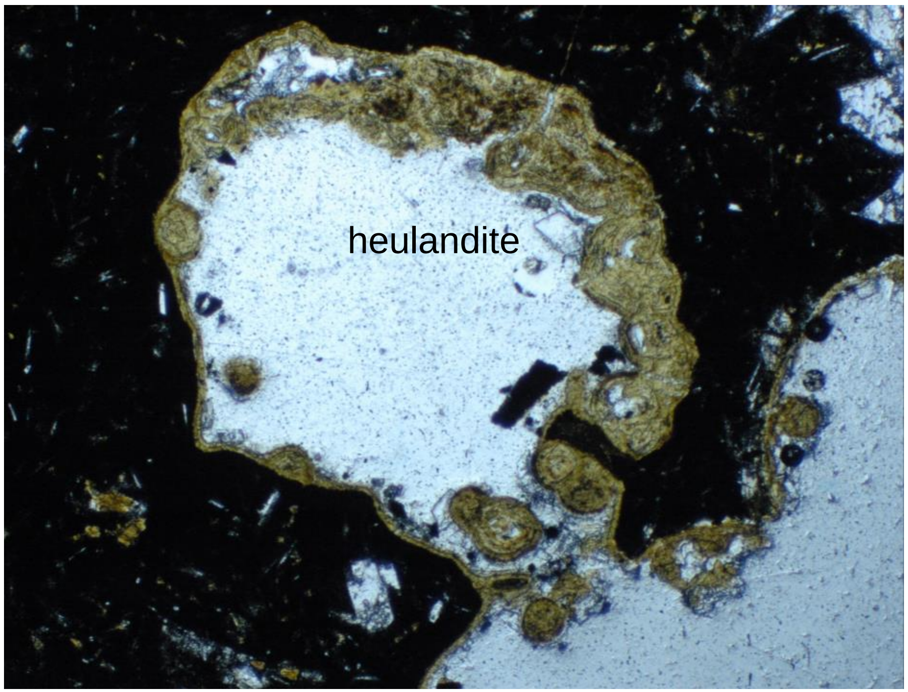
What does this mean for CO_2 sequestration in volcanic rocks?

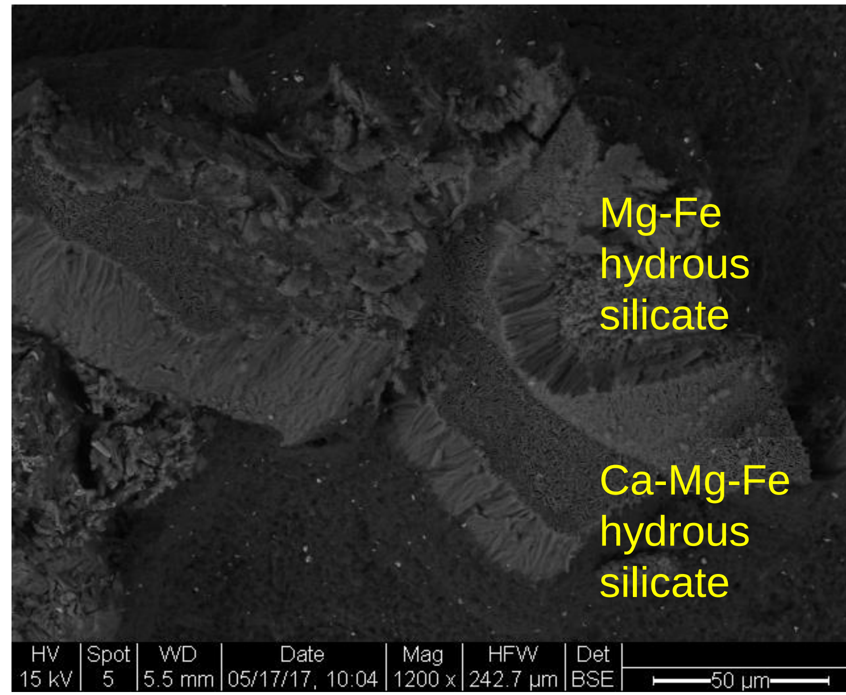




1. Characterization of the flow path geometry relative to the mineral distribution is key for predicting solute release behavior.

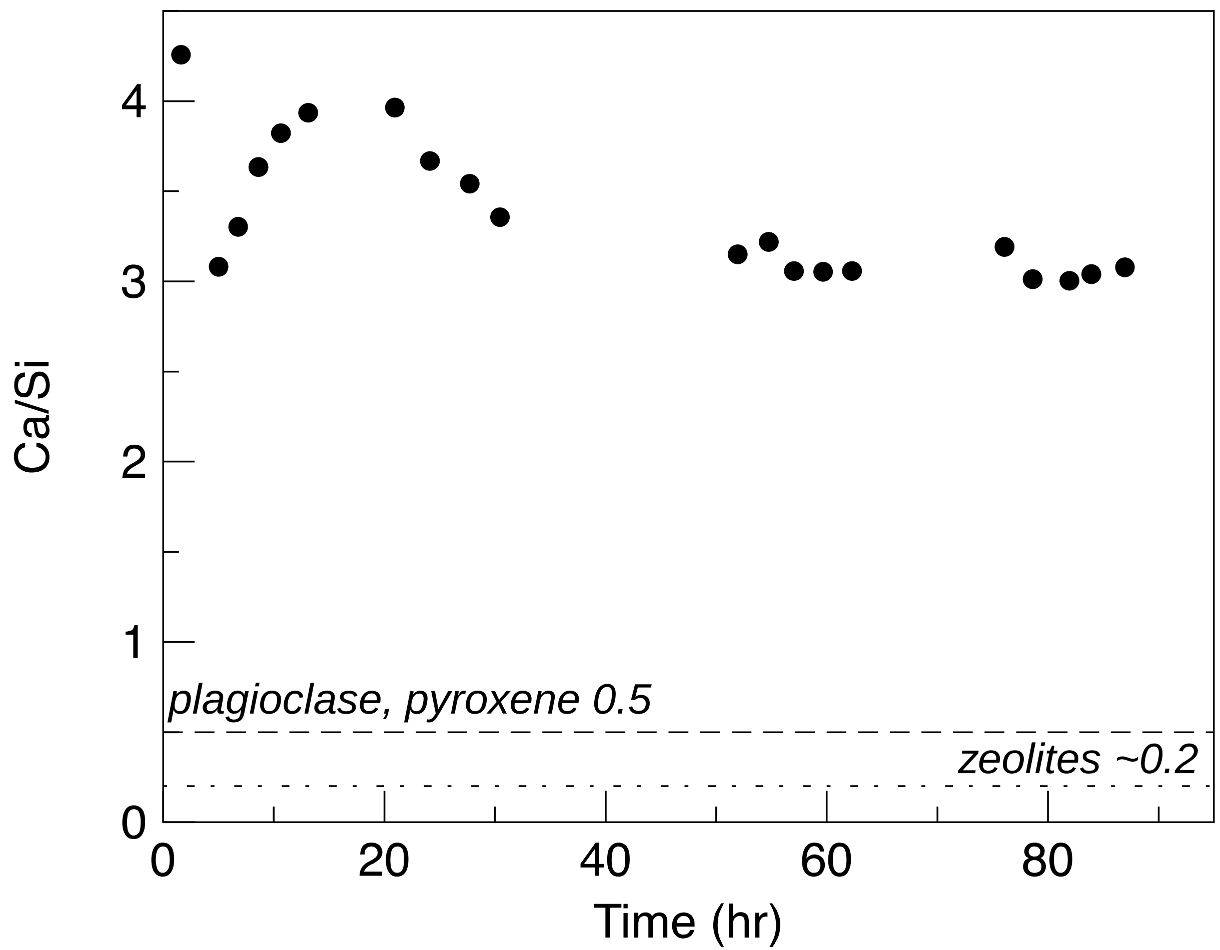
What does this mean for CO_2 sequestration in volcanic rocks?





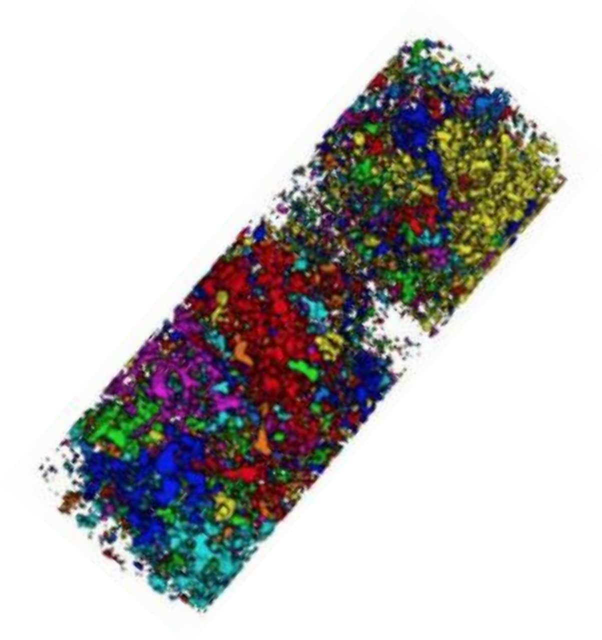
2. Ca-bearing zeolites may be an important additional cation source.

What does this mean for CO_2 sequestration in volcanic rocks?



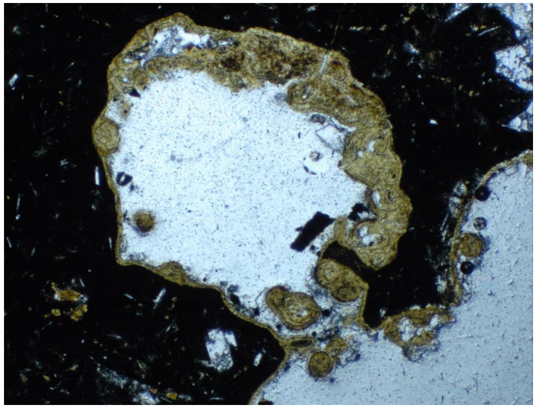
3. Addition of a supporting electrolyte (e.g. Na^+) could promote ion exchange and Ca^{2+} release.

Future work: improving models for mineral carbonation



Well-constrained batch experiments to obtain reaction rate information:

- Dissolution reactions
- Exchange reactions



Link results to flow experiments and evaluate against Carbfix results

- Reactive transport modeling
- Better predictive models

Thank you! Questions?

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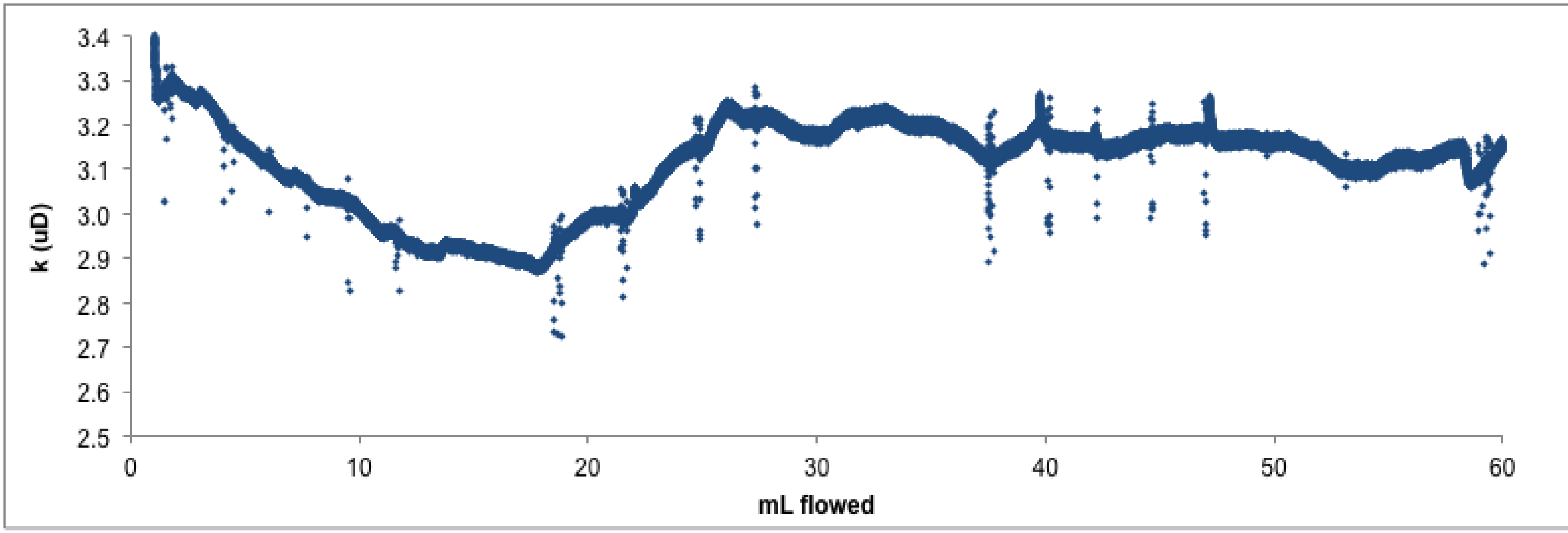
extra slides and figures

Despite dissolution and cation release, negligible changes in permeability



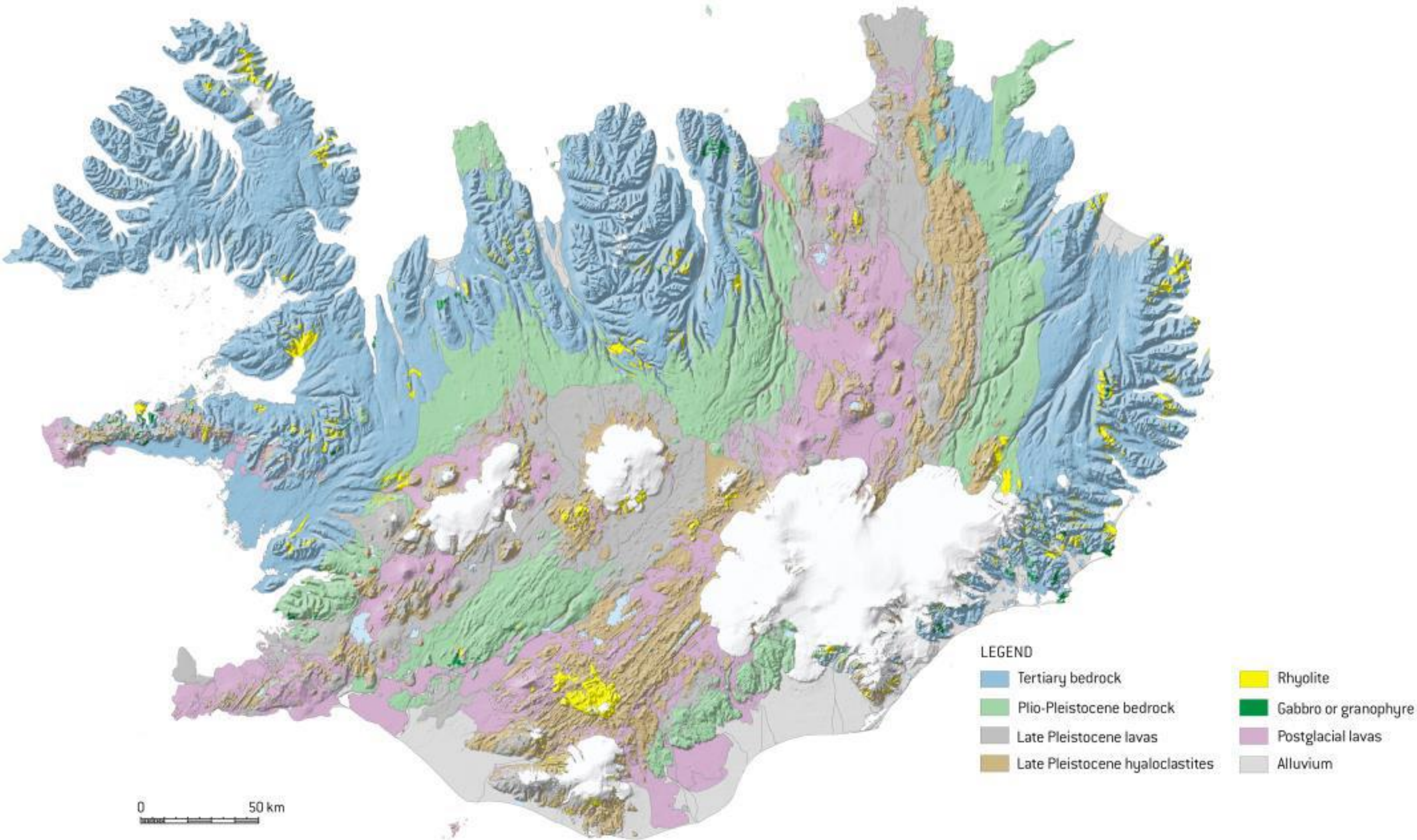
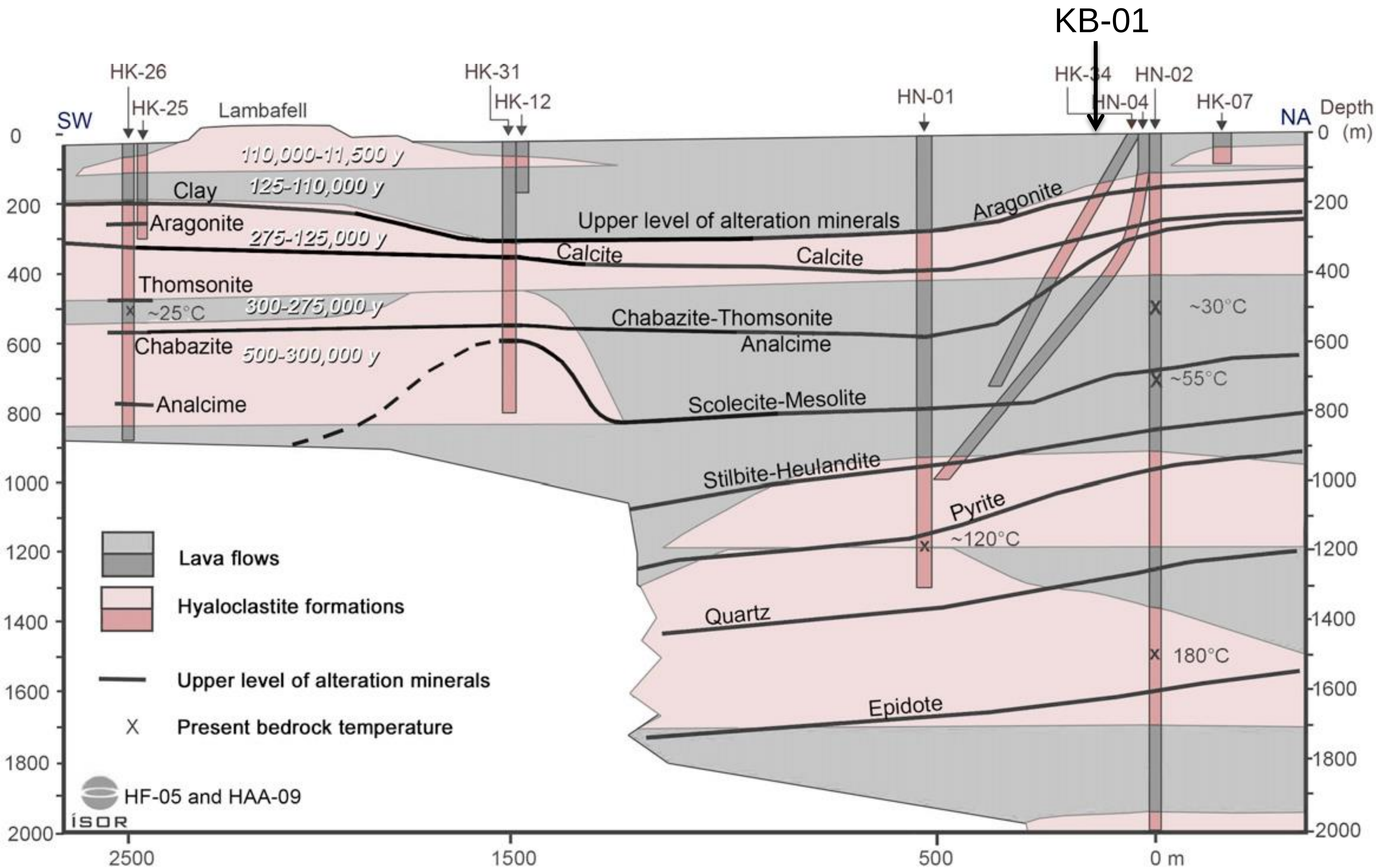


Fig. 3. Map based on Geological map of Iceland [18]. Iceland, 1:1.000.000. Icelandic Institute of Natural History.

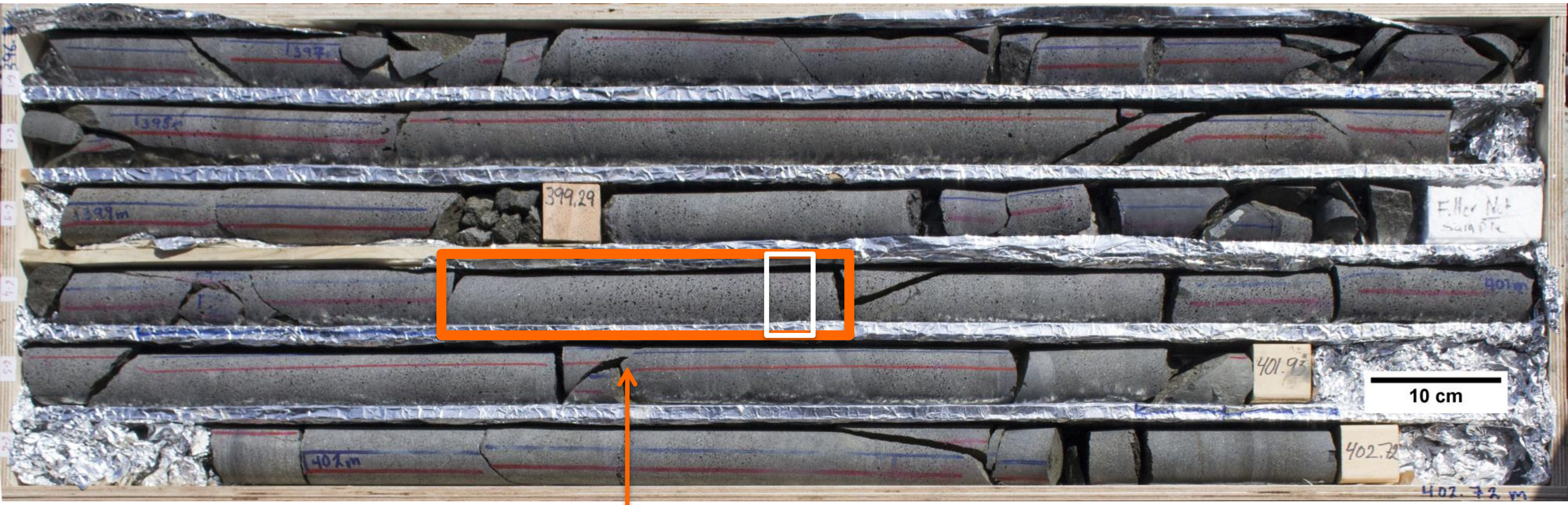
Snæbjörnsdóttir and Gislason, 2016

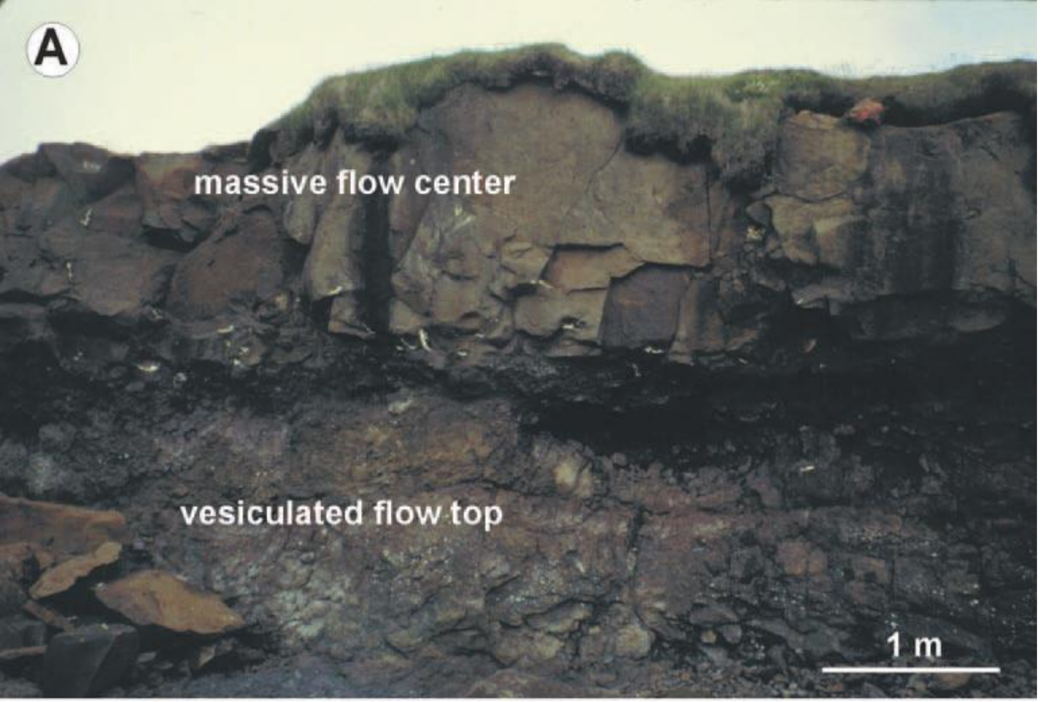
Fig. 11. Iceland and the Mid-Atlantic ridge. (Based on map from Amante and Eakins [56]).

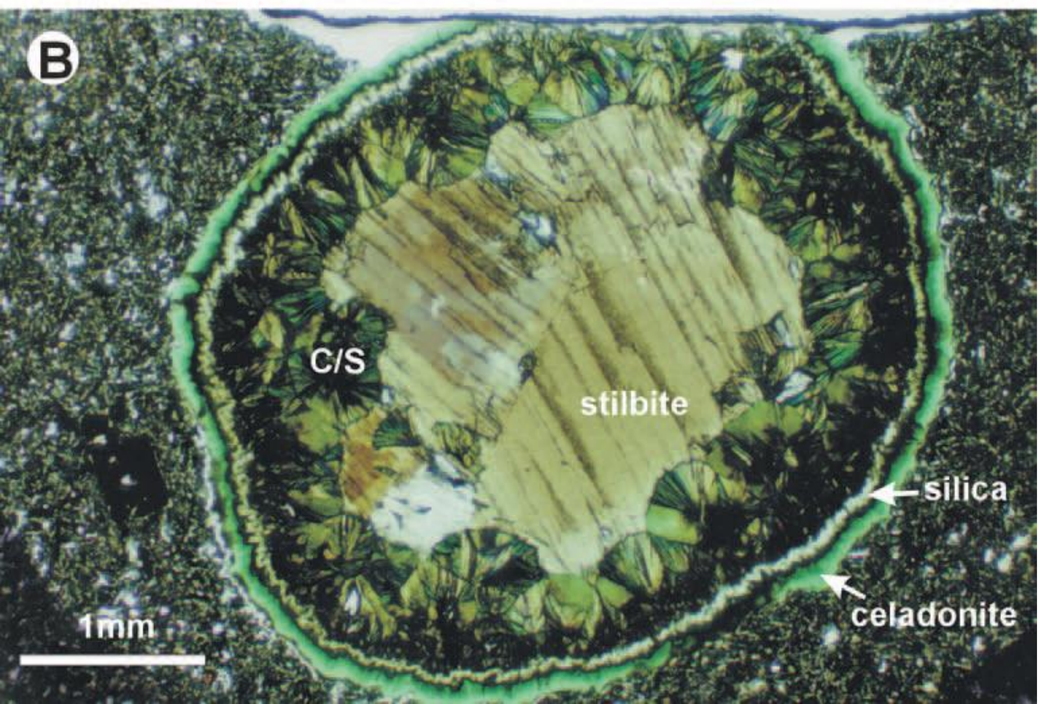
Snæbjörnsdóttir and Gislason, 2016



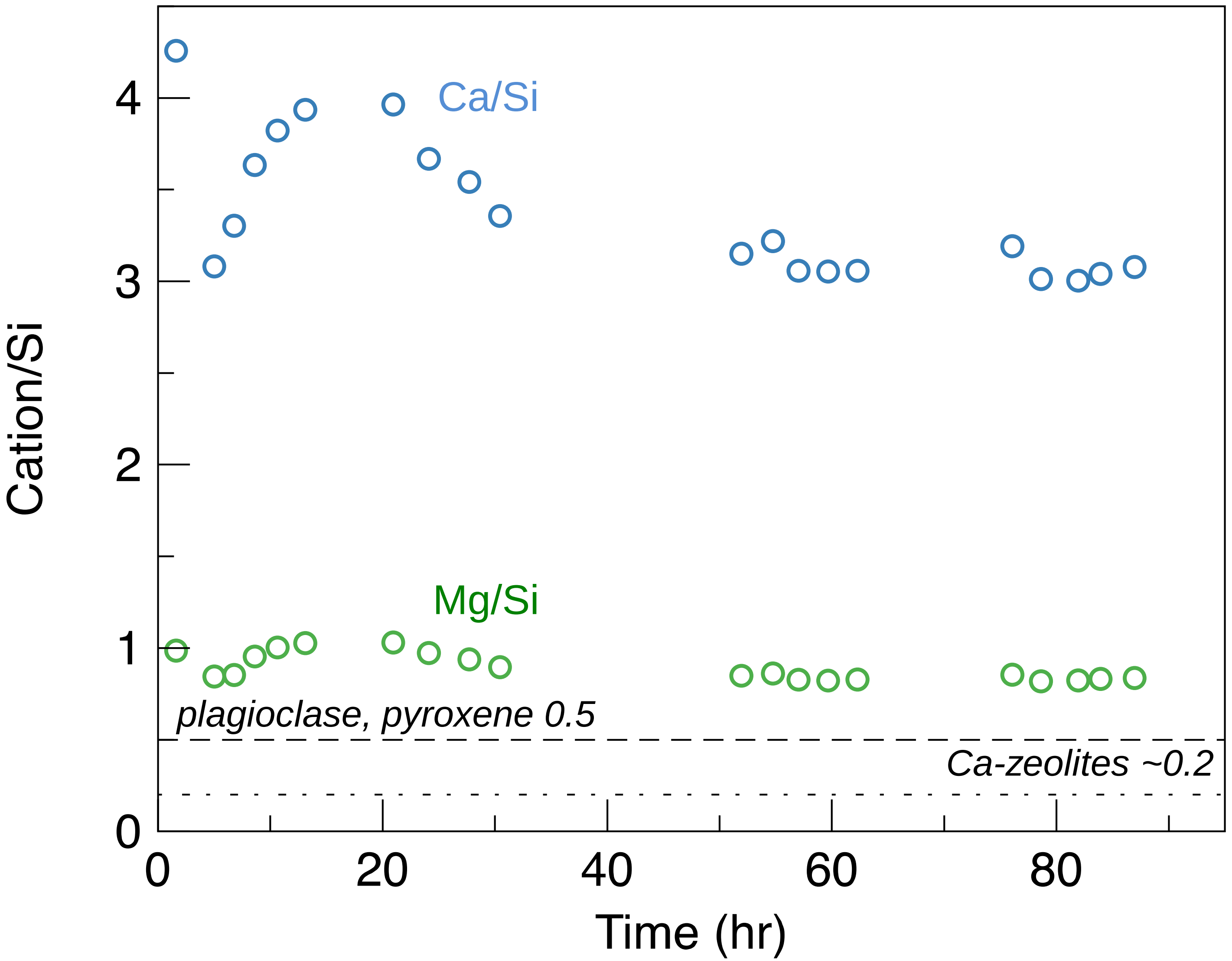
KB-01
HK-26
HK-25
Lambafell
HK-31
HK-12
HN-01
HK-34
HN-02
HN-04
HK-07
SW
NA
Depth
0 (m)
110,000-11,500 y
125-110,000 y
Clay
Aragonite
275-125,000 y
Upper level of alteration minerals
Calcite
Calcite
Thomsonite
~25°C
300-275,000 y
Chabazite-Thomsonite
Analcime
~30°C
Chabazite
500-300,000 y
~55°C
Analcime
Scolecite-Mesolite
Stilbite-Heulandite
Pyrite
~120°C
Quartz
180°C
Epidote
Lava flows
Hyaloclastite formations
Upper level of alteration minerals
Present bedrock temperature
HF-05 and HAA-09
ÍSOR
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2500
1500
500
0 m


10 cm

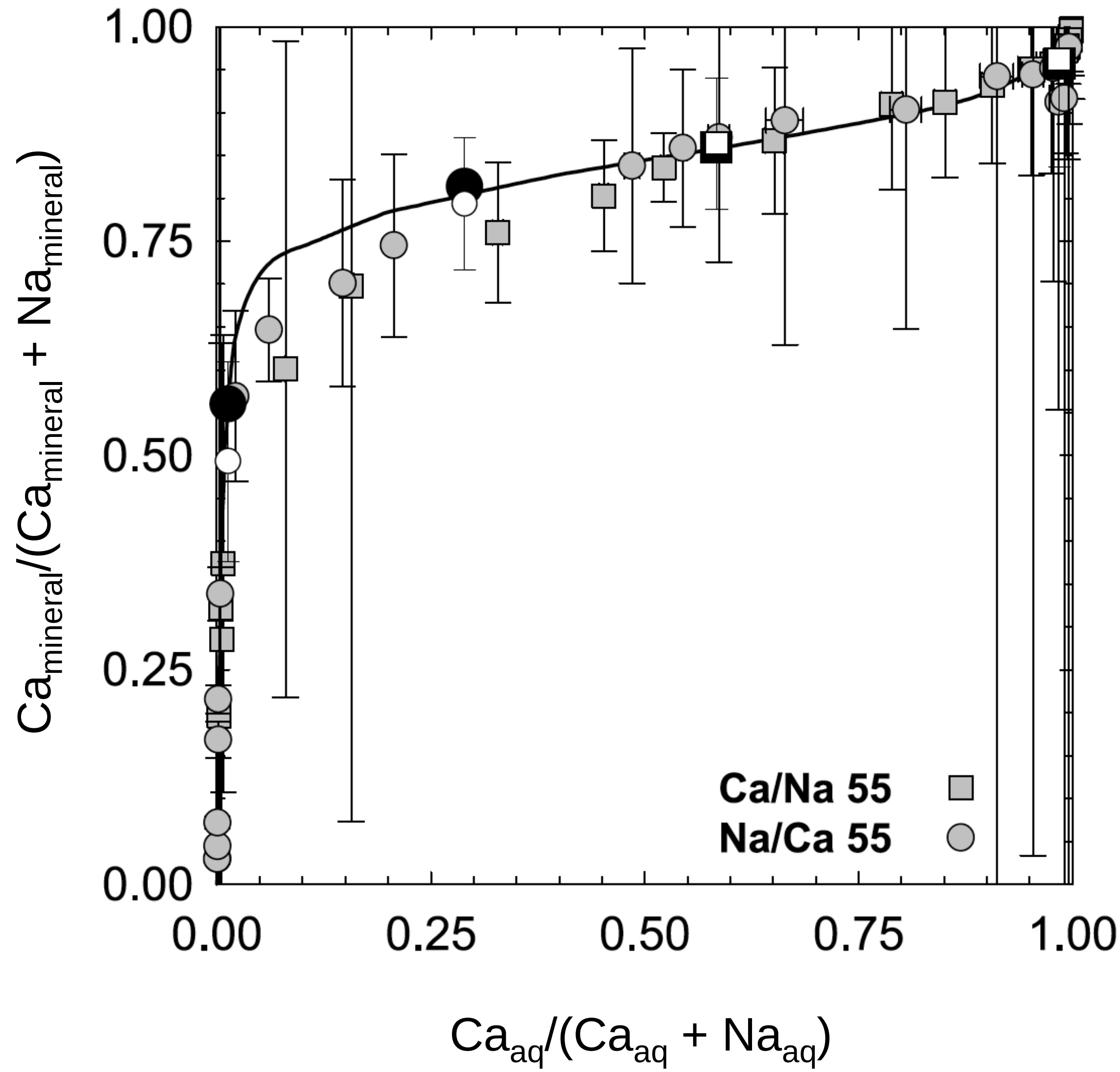




stilbite
$Ca_{4.5}Al_9Si_{27}O_{72} \cdot 24H_2O$

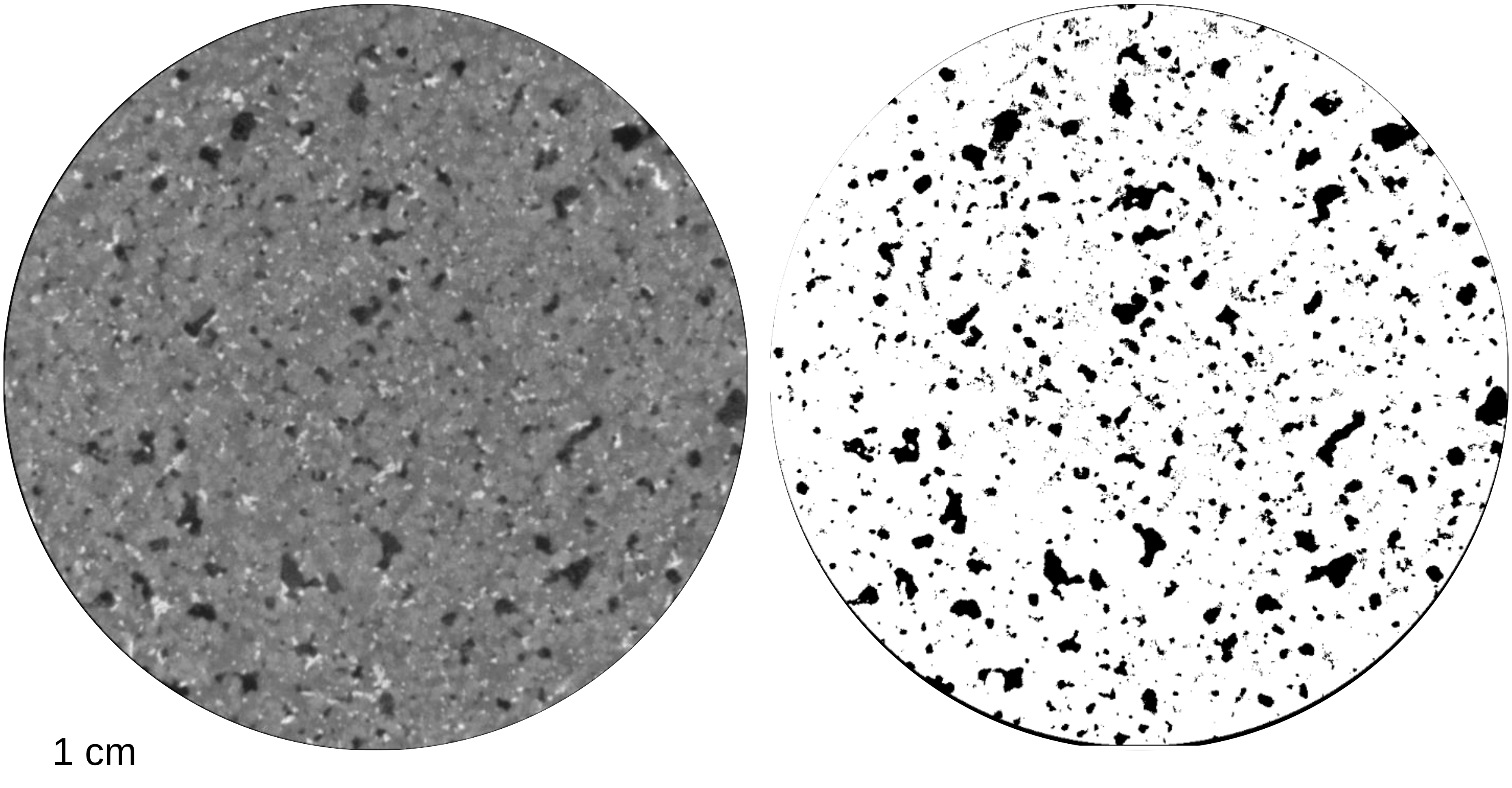


Ca/Si
Mg/Si
plagioclase, pyroxene 0.5
Ca-zeolites ~0.2
Cation/Si
Time (hr)
0
1
2
3
4
0
20
40
60
80

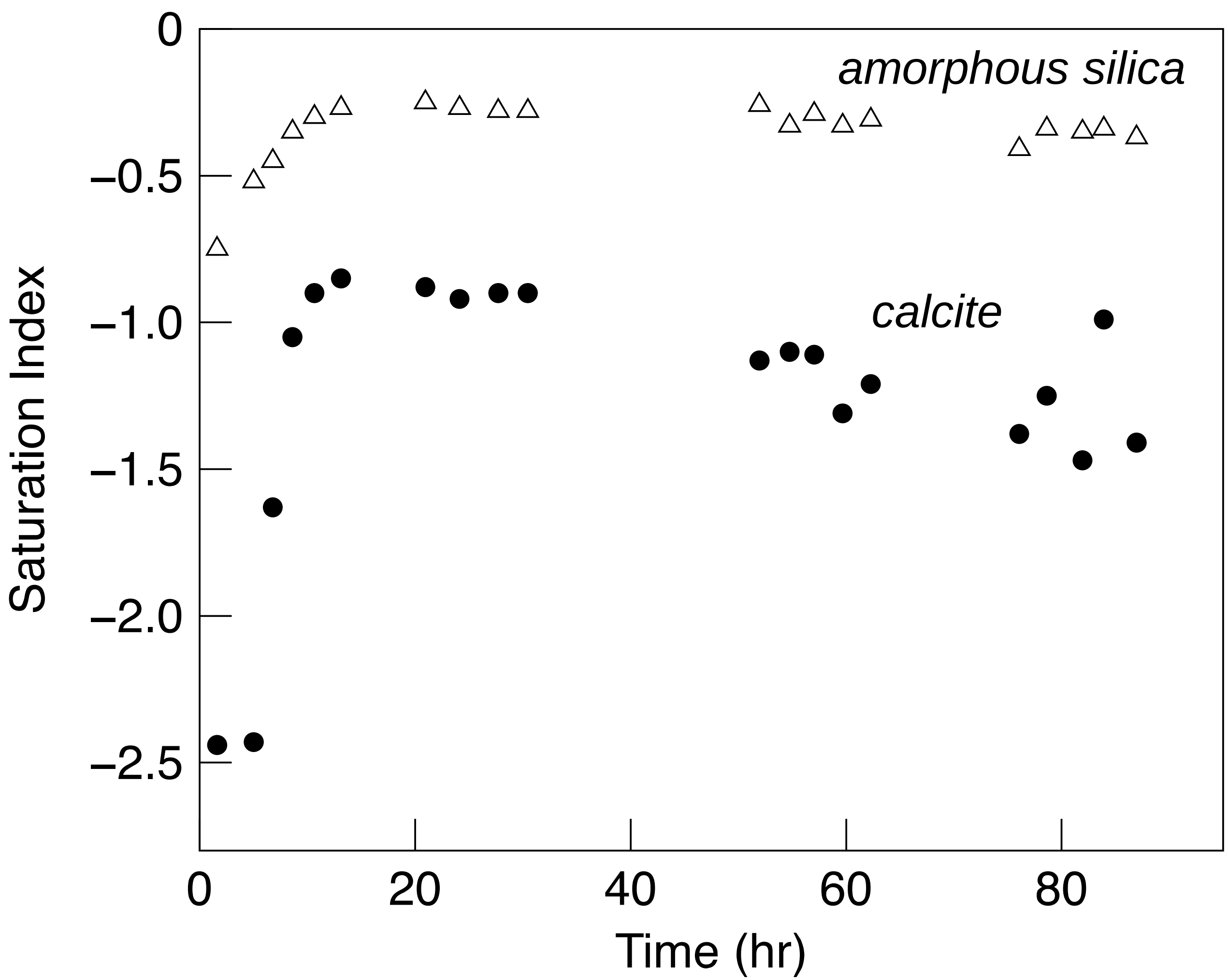


Ca-mineral + Na^{+} (aq)→ Ca^{2+} (aq) + Na-mineral

MicroCT imaging yields porosity estimates



Core-averaged porosity ~11%


0
–0.5
–1.0
–1.5
–2.0
–2.5
Saturation Index
0
20
40
60
80
Time (hr)
amorphous silica
calcite

Calculating dissolution rate

$[SiO_2]_{in}$

$[SiO_2]_{out}$

$$[SiO_2]_{out} - [SiO_2]_{in} = \Delta SiO_2 \text{ (mmol/L)}$$

"Effective dissolution rate" (mol/sec) =

aqueous concentration [mol/L] * volumetric flow rate [L/sec]

$$r = \Delta SiO_2 * Q$$