LAWRENCE LIVERMORE NATIONAL LABORATORY

The Role of Chemical Alteration in Arkosic Reservoirs

2023 FECM / NETL Project Review

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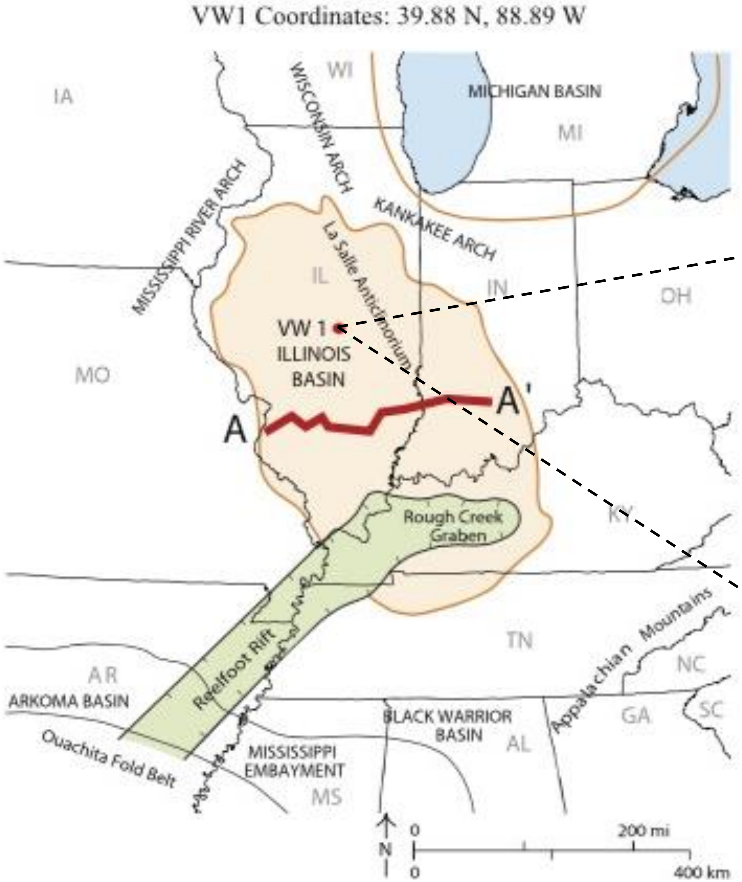
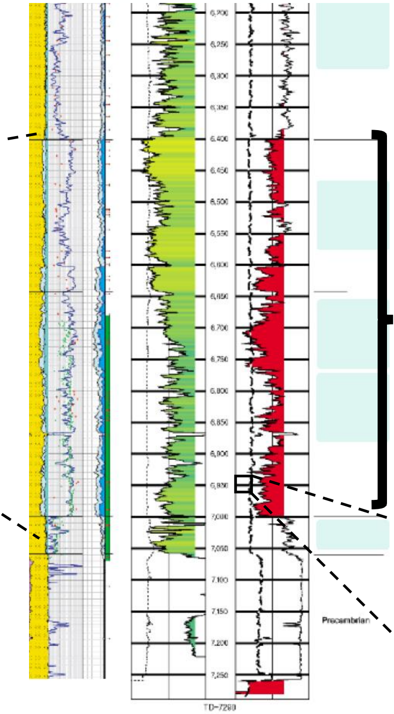
The (Lower) Mt. Simon sandstone is a remarkable storage formation – how will CO_2-induced mineral reaction impact its properties?



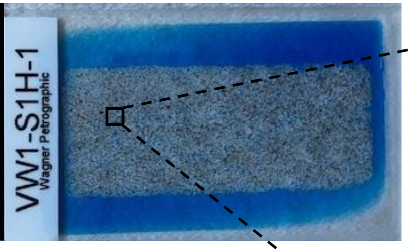


map: Labotka et al., 2015
column: Freiburg et al., 2022

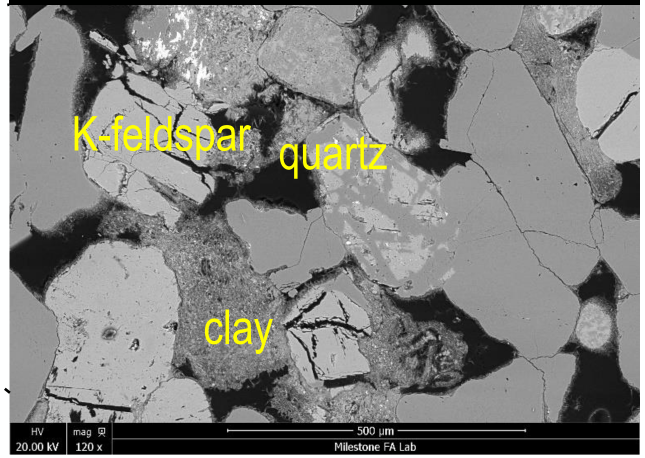
DOE, ISGS, and the CarbonSAFE program identified the Lower Mt. Simon sandstone for large-scale GCS based on exceptional porosity and permeability.

CO_2 injection perturbs its chemical equilibrium, forming high-surface area clays, which may clog pores or change reservoir properties.

Thin Section

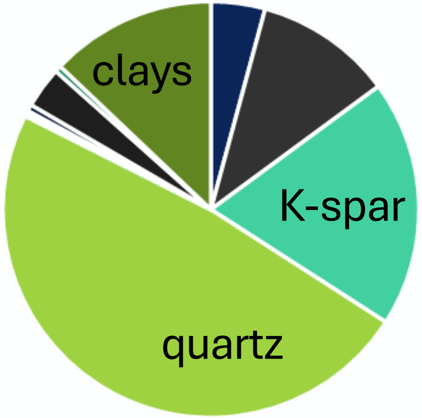


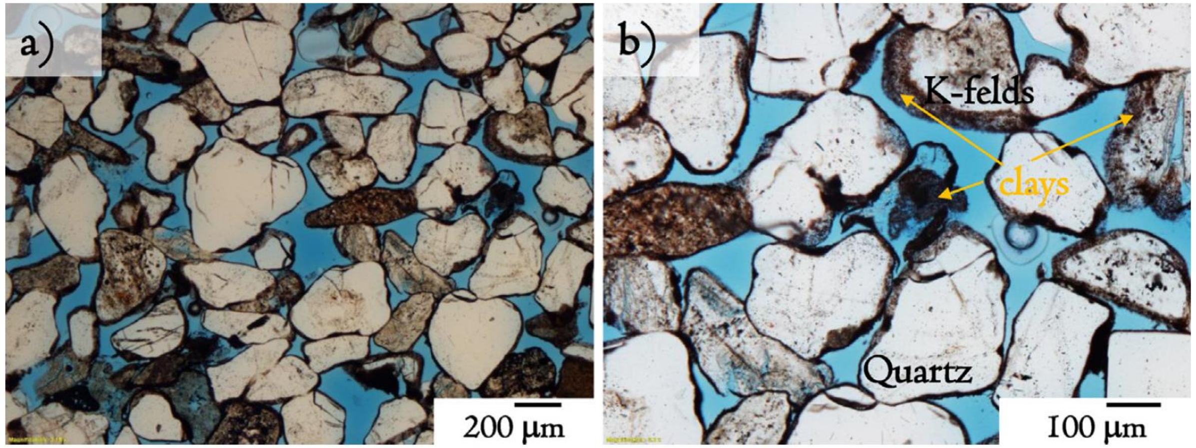
Scanning electron microscope (SEM)



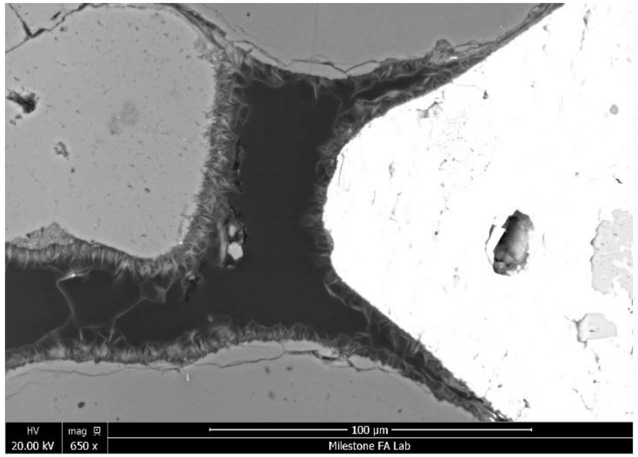
K-feldspars and secondary clays are reactive under high $p\mathrm{CO_2}$ conditions. These reactions could degrade pore space and/or permeability.

Chemical reactions among supercritical CO_2, brine, and the high surface area feldspars and clay coatings found in the Lower Mt. Simon pose an **important but poorly understood threat to CO_2 injection and long-term storage capacity.**

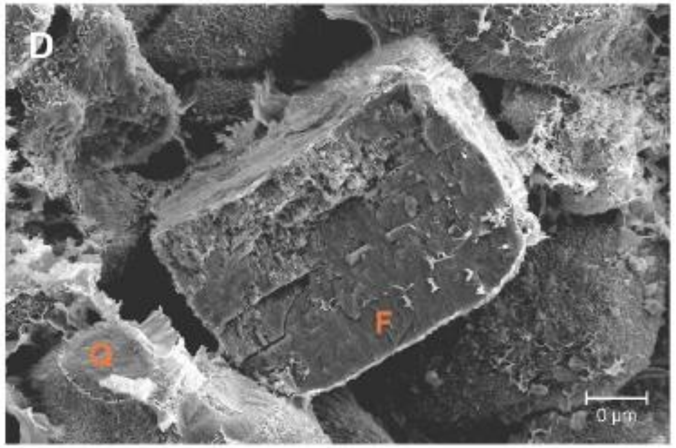




photomicrographs: Dávila et al., 2020



this work

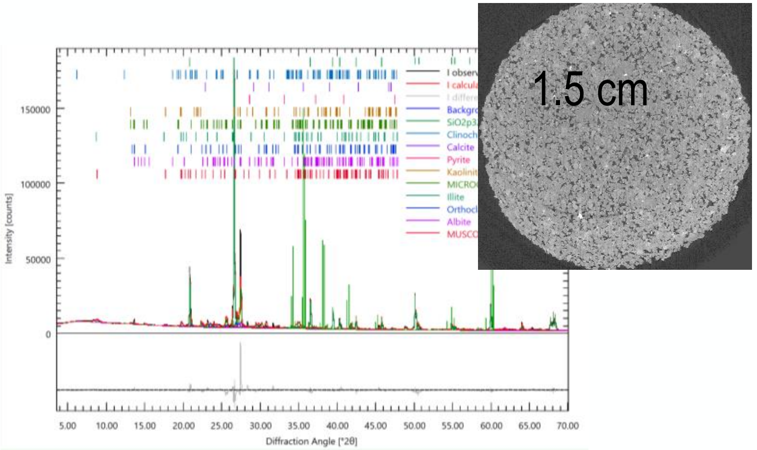


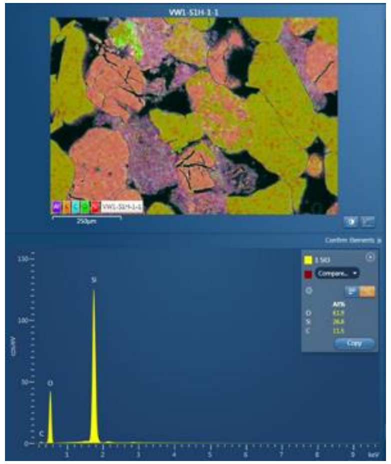
Freiburg et al., 2022

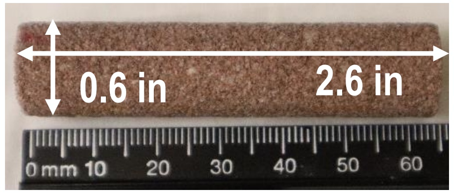
The project objective is to quantify the effect of chemical alteration on CO_2 injection in arkosic sandstone reservoirs.

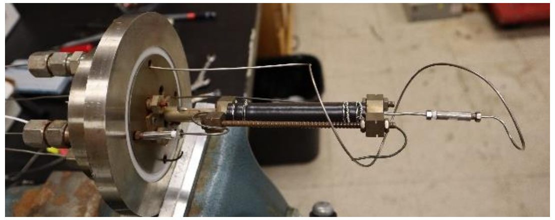
To do this, we utilize:

- detailed characterization of reservoir samples and solution chemistry
- core-flow experiments at relevant conditions
- reactive transport modeling

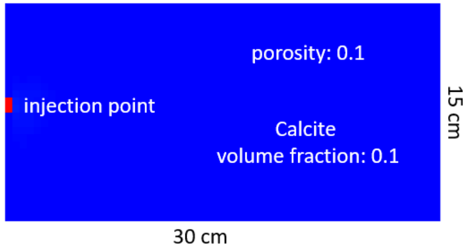


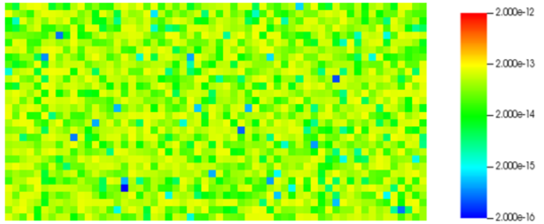






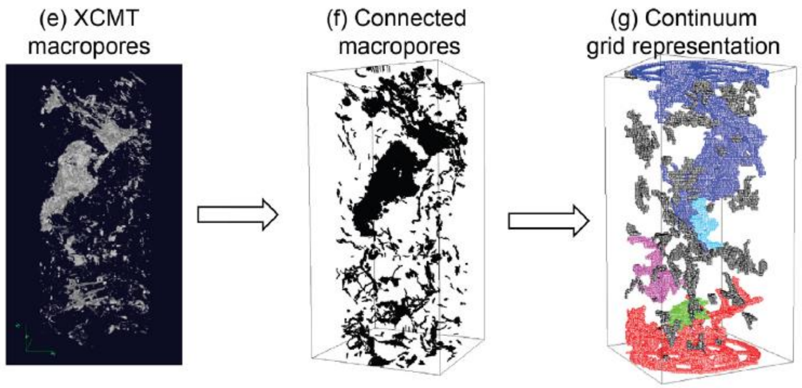
The project deliverable is an experimentally calibrated reactive transport model of this important reservoir, to help answer the question of whether chemical alteration negatively affects the CO_2 storable quantity within the Lower Mt. Simon.



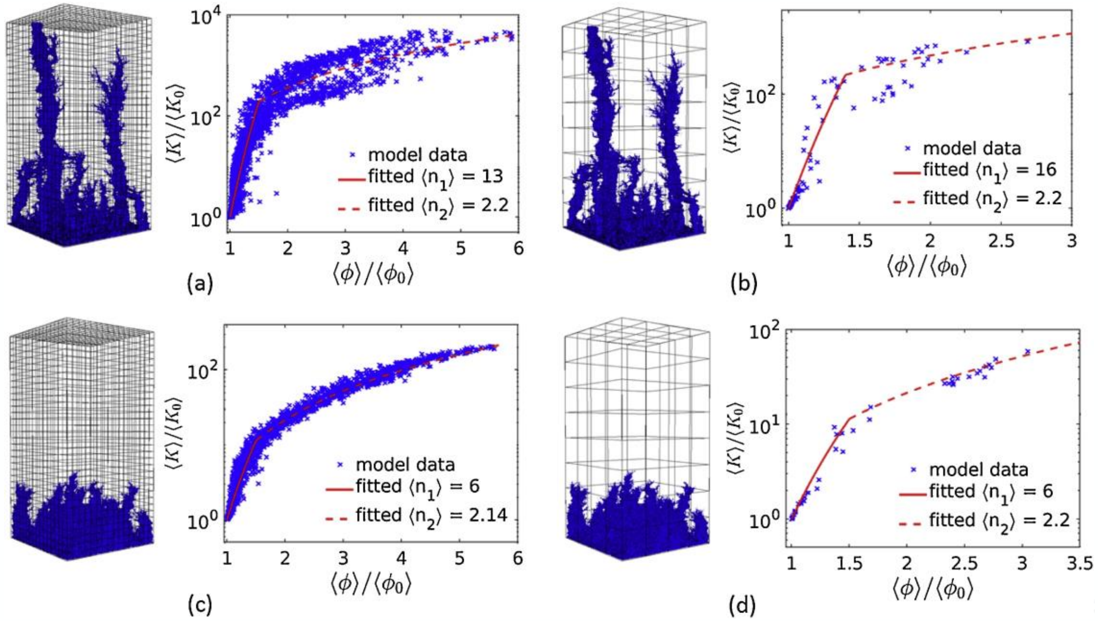


This project leverages LLNL core capabilities and workflows developed under previously DOE-supported projects.

An earlier study of CO_2 reactivity in carbonate cores from the Weyburn-Midale CCS project yielded efficient methods for resampling high-resolution computed tomography data to initialize a continuum model (Carroll et al., 2013)



We utilized LLNL's parallelized HPC resources to numerically investigate the scale dependence of key transport and reaction parameters using micron-to-meter-scale upscaled models (Hao and Smith et al., 2019)



Current progress

Core-flooding experiments

7 experiments completed. *2 publications in preparation. 2 remaining experiments planned for October 2023.*

Analysis of alteration

Solid and solution chemistry analyses complete; pre-reaction CT data acquired and processed; post-reaction CT data acquired. *Digital image correlation slower than anticipated due to registration challenges.*

Development of reactive transport model

Initial chemistry model derived in CrunchFlow; reactive test cases run using NUFT; *calibration and integration is focus of final year*

Experiments focused on the impacts of residence time, brine salinity, and transverse bedding

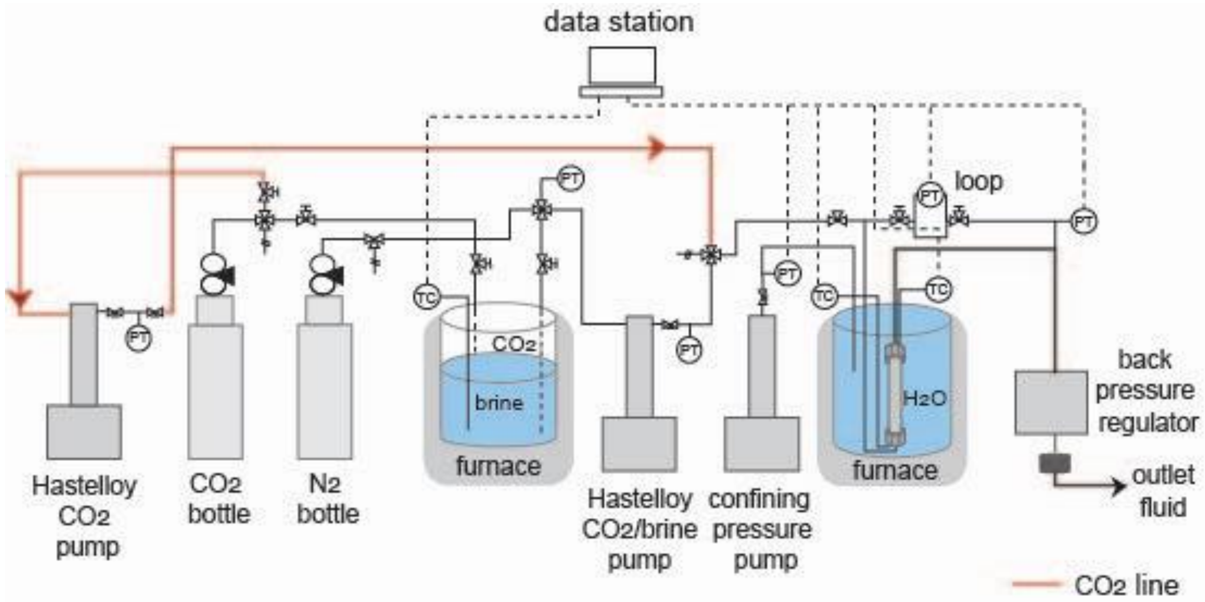
Experiments conducted at 60°C, 25 MPa confining pressure, using 2M NaCl brine and ~5 MPa *p*CO_2

2021 Flowrate varied from slow, to intermediate, to fast (over equal number of pumped pore volumes)
manuscript in preparation

2022-23 Brine salinity varied over 2 orders of magnitude (at intermediate flowrate)

2023 Vertical vs. horizontal permeability assessed (at intermediate flowrate)

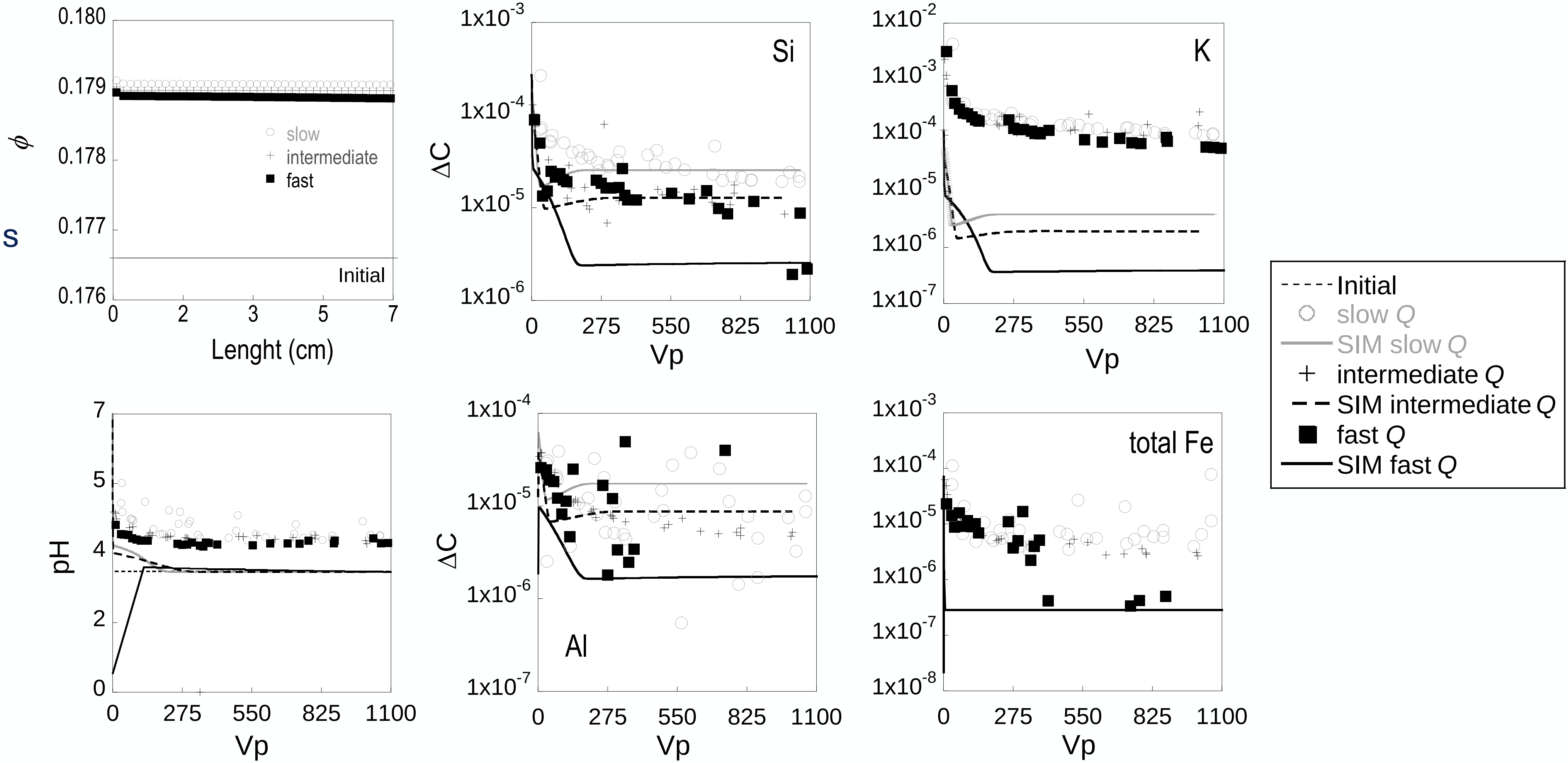
2023 wet scCO_2 and multiphase experiments planned



Varying flowrate influences the *extent* of mineral-CO_2-fluid reaction

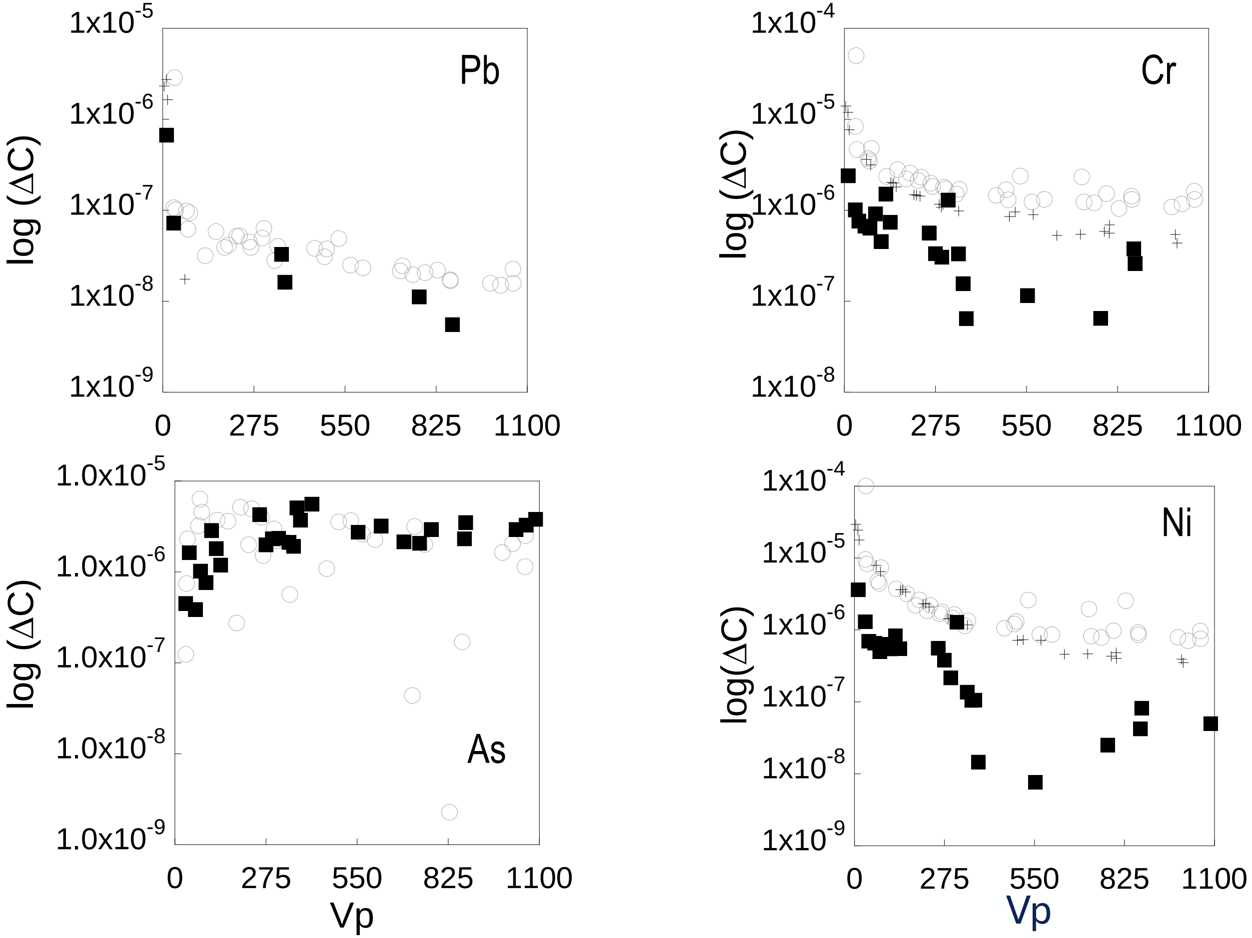
As expected, dissolved concentrations increase as residence time increases.

Preliminary simulations using literature values for reaction rate and surface area do not represent [K^+] well at all



Dávila et al., 2023 (in prep)

Similar to Shao et al.'s (2020) batch studies, we also note metal releases

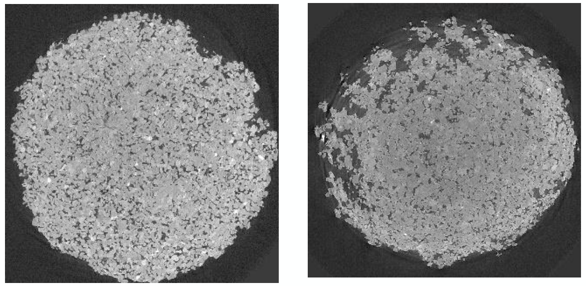


[As] exceeds regulatory limits, but this finding should be viewed in the context of the background concentration of metals present in resident brine.

Dávila et al., 2023 (in prep)

Post-reaction imaging demonstrates changes to mineral and pore structures

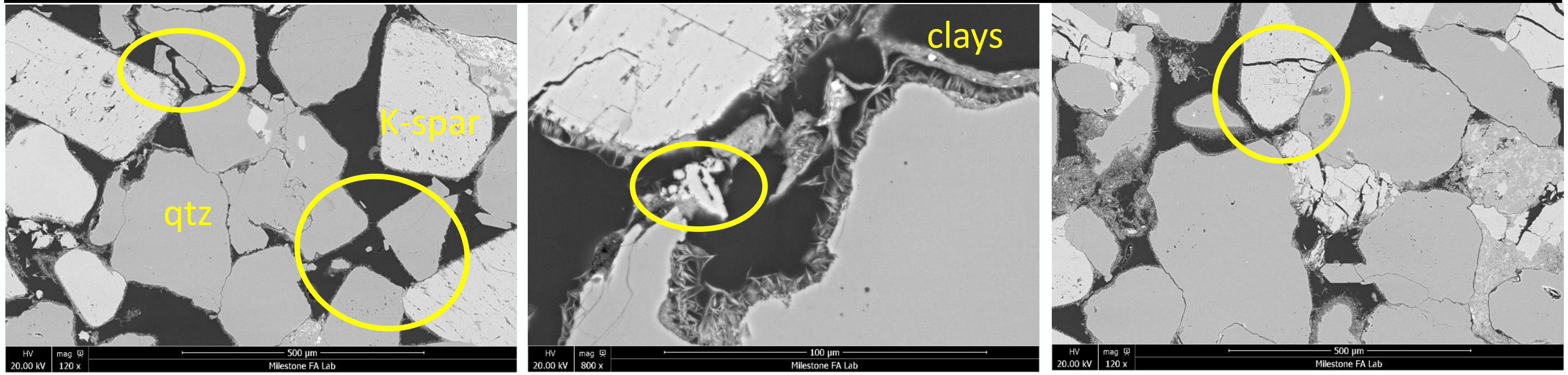
1 cm downstream of inlet



(pre)

(post)

Representative post-reaction textures and features



dramatic porespace increases confined to near-inlet

wholescale removal of pore-lining clays visible at finer-scale

newly formed X-ray bright (Fe-bearing?) small solids

appearance of newly “detached” grains → challenging for image registration, correlation

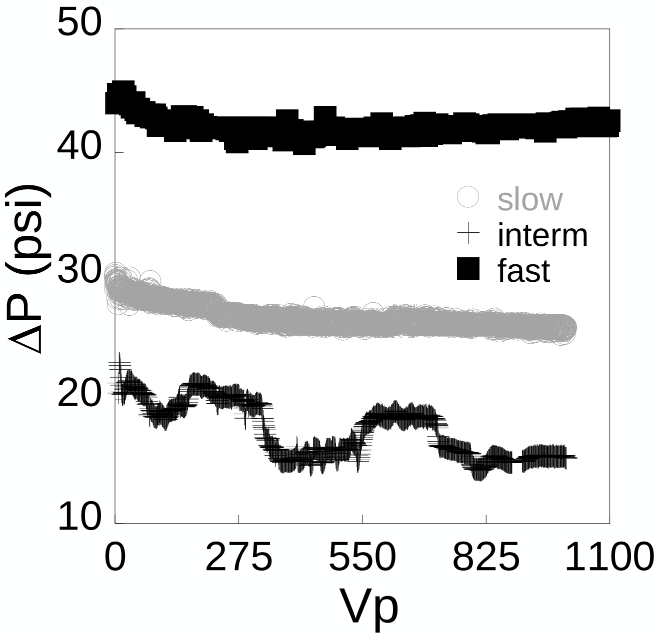
Despite observations of mineral reaction, porosity change, and grain shifting, **sample permeability remains largely intact**

Overall, we observe no change in permeability for the fast flowrate case, and slightly increasing permeability for intermediate and slow flowrates.

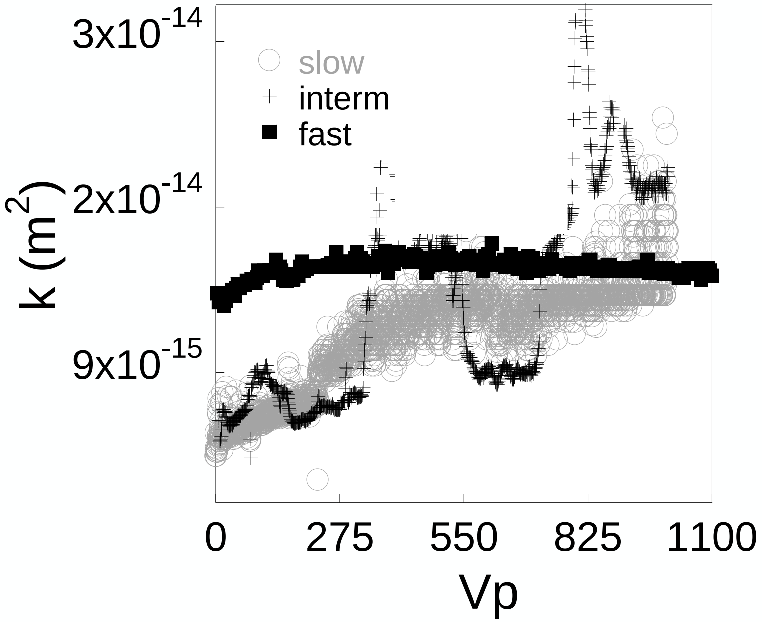
This is not bad news

Could migrating particulates/fines be responsible for the pressure variations observed in the fast flowrate case?

Testing this idea with average grain size analysis.



Note small y-axis range



Dávila et al., 2023 (in prep)

How can we adapt our chemical model to better represent the trends that we observe?

Underprediction of dissolved silica

increase mineral reaction rates, or increase mineral surface area

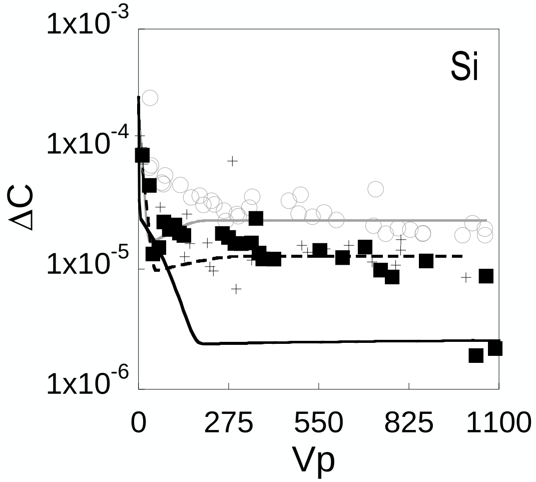
[Na+] uptake/preferential [K] release within first 50 pore volumes

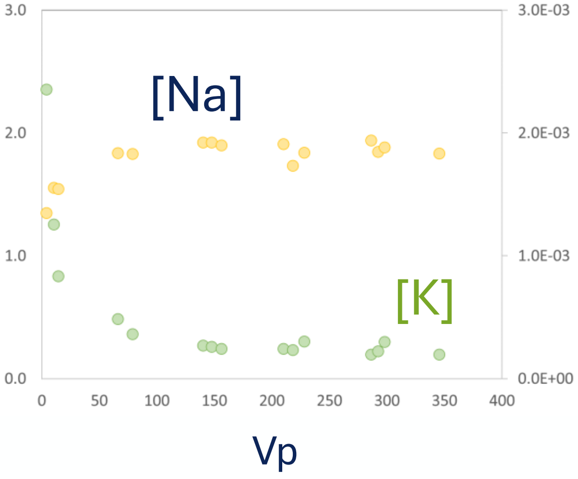
presumably due to ion exchange by clays, likely necessary to capture trends in K/Na ratios

Al/Si ratios indicate incongruent dissolution of >1(?) mineral phase

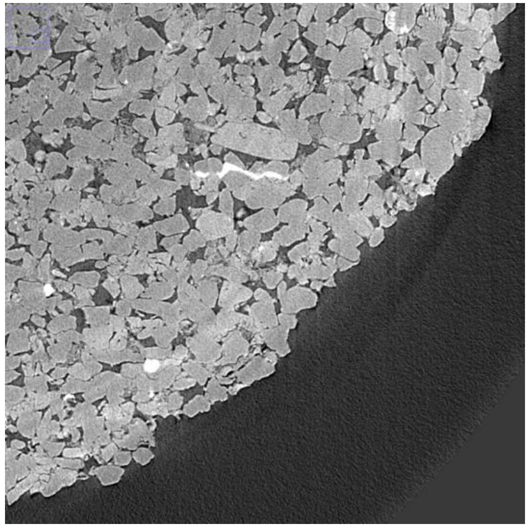
can incorporate "non-ideal" stoichiometry model phases

How much detail is needed depends on the application, the user's need, and observations from the larger-scale





The resolution of the CT imaging limits what we can extract from it – but it also provides statistical support for a larger REV



The difference in gray-scale between quartz and feldspars is <6% of the greyscale range.

Clay linings are not statistically distinguishable from pore/void space within the XRCT greyscale.

Grain size analyses, pore distributions, and bulk porosity are useful outputs from these image sets – but require careful registration!

Grain shifting occurs throughout these samples - digital image correlations (DIC) attempts are currently carried out in batches, on very thin (i.e., <1-mm) image stacks

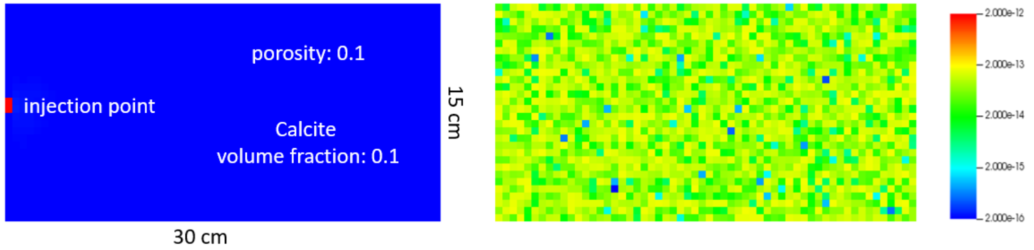
What are the implications and next steps for model development?

- We continue to use reactive transport code NUFT to winnow the *necessary* chemical processes from the full suite of possible reactions
- We use fewer/larger grid blocks/nodes due to these samples' relative physical homogeneity and we will remain at 2D
- **We will draw on scripting and statistical expertise at LLNL to 1) efficiently create multiple model initializations that sample our parameter ranges, and 2) batch these runs for use with existing bank time**
- **We are applying for additional computing resources to accommodate better statistical sampling; awards announced January 2024**

$$k_{(t)} = f(\theta)$$

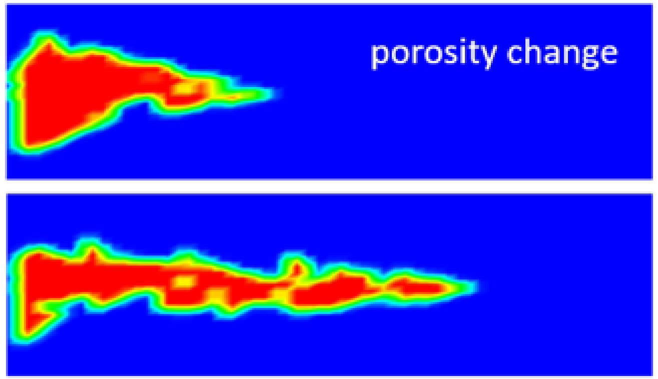
$$R_m = A_m \sum_{terms} k_{m,T} a_{H+}^{n_{H+}} \left(\prod_i a_i^{\,n_i} \right) \left(\left(\frac{IAP}{K_{eq}} \right)^{m_2} - 1 \right)^{m_1}$$

2D Simulation of Mineral Dissolution



model domain

initial permeability



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