SAND2021-14126PE

NUCLEAR WASTEFORM AND BARRIER MATRIX INTERACTIONS WITH GEOLOGIC STRATA IN THE SUBSURFACE OF THE YAMIN PLATEAU, NORTHERN NEGEV, ISRAEL

Progress Update – November 2021

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Presentation Outline

- Objectives
- Expected Contribution to Intermediate Depth Borehole (IDB) Design and Safety Case
- Project Approach
- Model and Simulation Results
- Experimental Work & Preliminary Results
  - MicroCT
  - Sample Preparation
  - SEM/EDS
  - Nano & Micromechanical Testing
- Relating Experimental Data to Simulations
- Future Direction

Objectives

Project goal: Characterize interactions of doped cement materials (Low pH cements and CEM I) with carbonate geologic strata within the Mount Scopus Group (i.e., limestone, marl, chalk, oil shale) of the northern Negev, Israel.

Specific objectives:

i) Use laboratory experiments to characterize the reactions and transport of radionuclides (dopants) and primary matrix constituents at the interface between carbonate rock types and cementitious barriers; and,

ii) Demonstrate and benchmark multiphase diffusion reactive transport models for parameter estimation and to simulate long-term interactions considering potential intermediate depth borehole disposal.

Expected Contribution to IDB Design and Safety Case

- Guide the selection of the chemically appropriate cement formulation for the host rocks in Israel
- Provide mechanistic basis and validated models for reactions and diffusive mass transport at representative rock-cement interfaces
- Define expected contaminant migration factors (e.g., effective R and K_d) from cement waste form to rock formation
- Provide input on the safety margin for unsaturated cement environment (strength, formulation and migration)

Project Approach

Rocks and cement characterization – ***porosity, mineral assemblages***

1313 tests (L/S = 10 and 1 over range of pH) – ***calibration of mineral reaction set***

1315 tests (diffusion) – ***calibration of tortuosity, verification of mineral reaction set***

measured

Completed

Data from cement/rock interface experiments

planning

Cement/rock interface modeling - prediction

measured

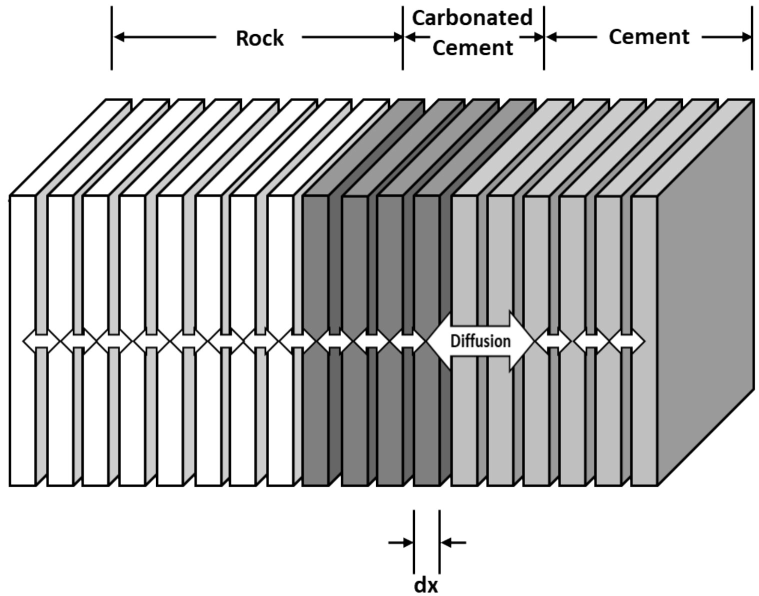
comparison

Solids characterization – micro-CT, Nano-indentation, SEM, LA-ICP-MS

Interface Evaluations

- 6 rock types, each with 2 cements
- Experiments – ca. 1-2 years
- Simulations
  - Experimental planning
  - Experimental data interpretation
  - Long-term prediction

Conceptual Model – Rock/Cement Interface



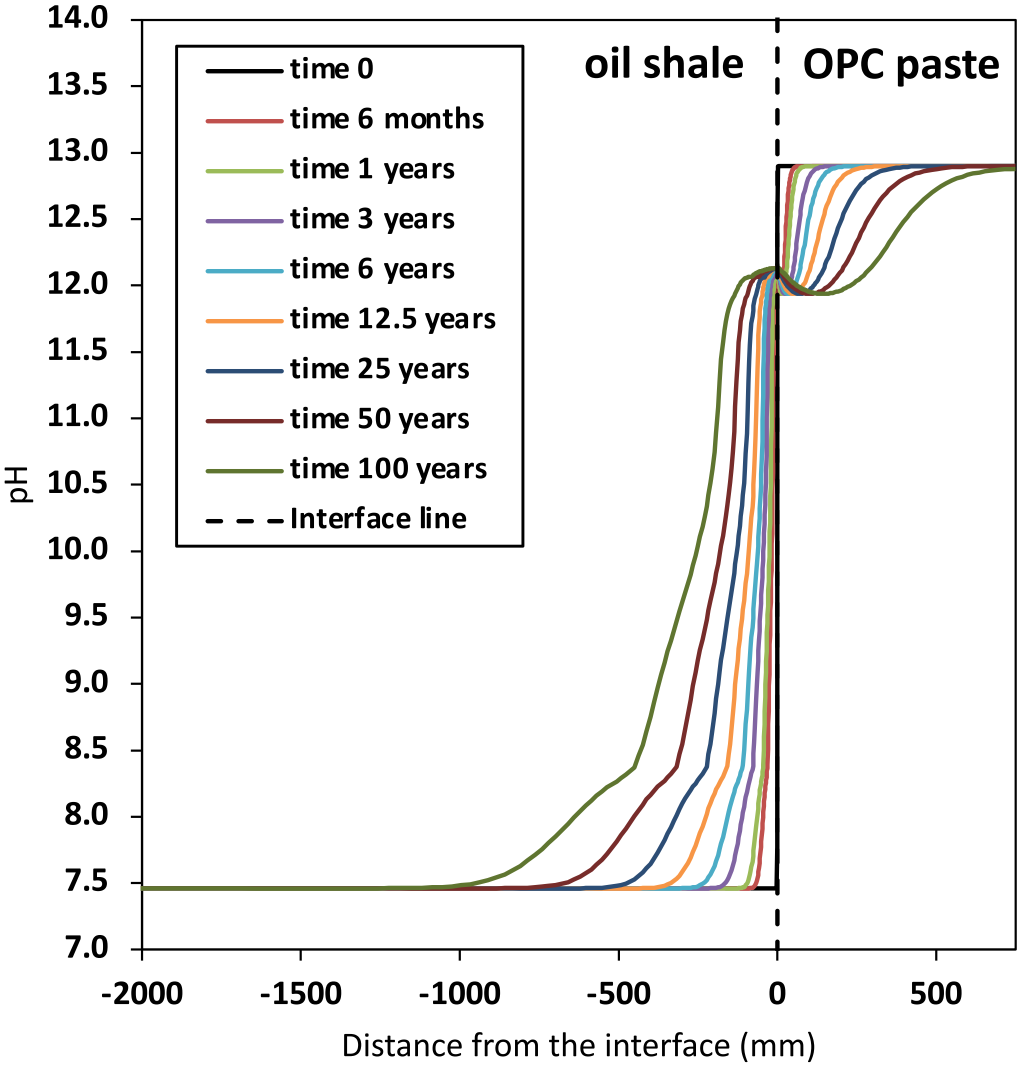
Model assumptions:

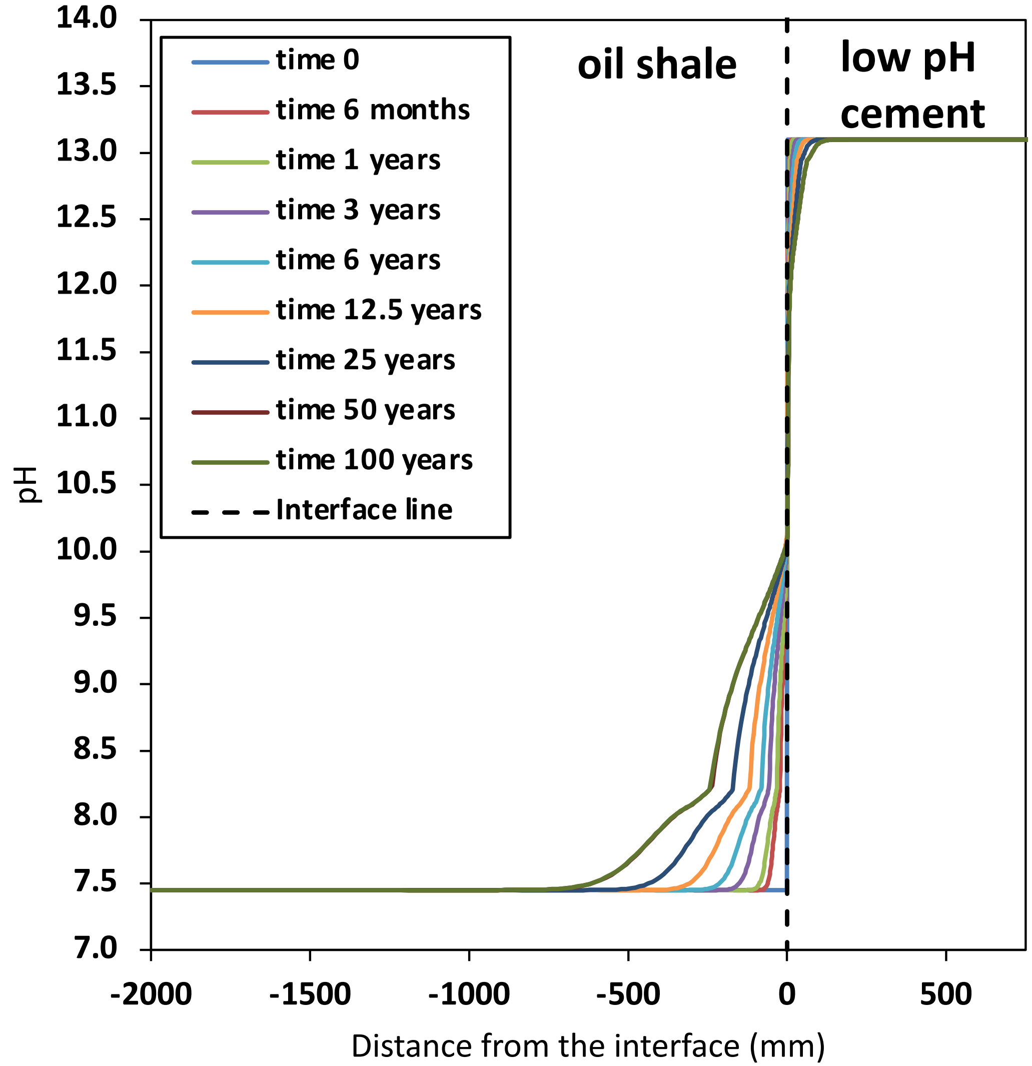
1. Each cell is well mixed
2. Local equilibrium
3. C-(N-)A-S-H solid solutions
4. Multi-ionic diffusion only
5. Materials intact throughout the entire simulation

Model conditions for experimental case:

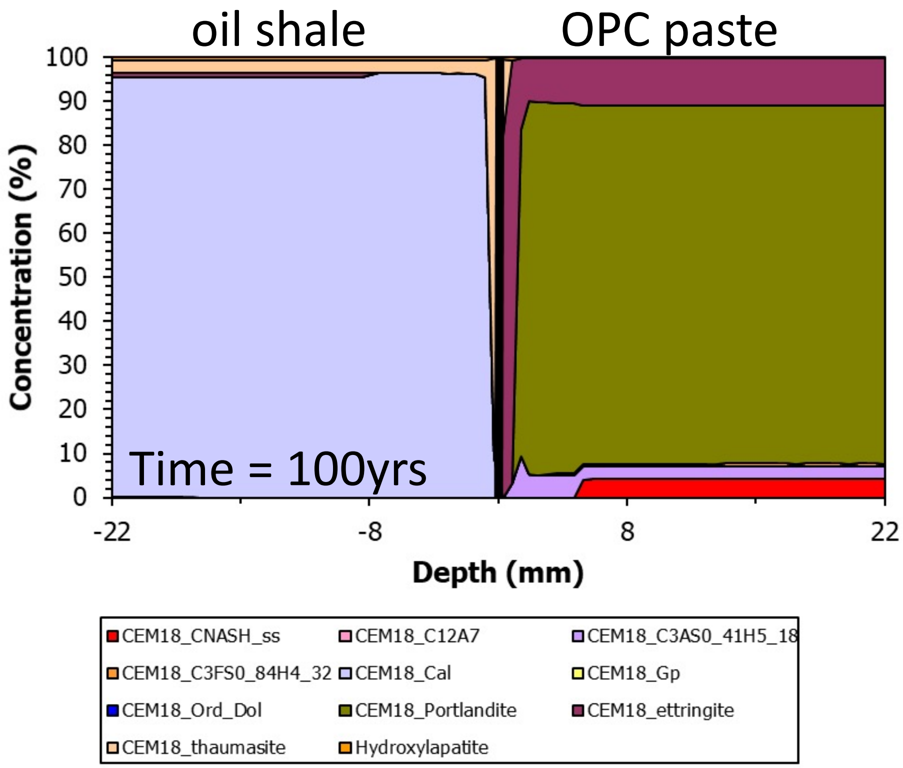
- 100 years simulated, saturated conditions, 30 C
- 1-D, 378 cells, Finite volume
- No fluxes at external boundaries
- Thermodynamic databases – Minteq v4; LLNL, CEMDATA18 (Lothenbach et al. (2018))
- Initial carbonate content – based on 1313 test
- Tortuosity – calibrated values
- Porosity – measured values

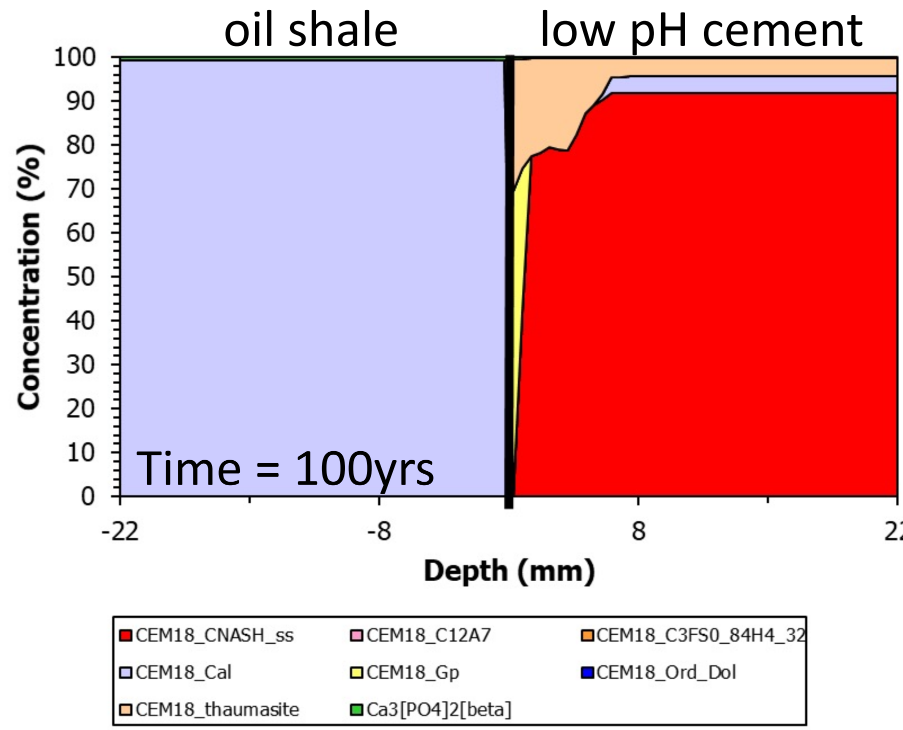
Simulations Results – pH Profiles





Simulation Results (100 yrs) – Solid Phases Distribution Profiles





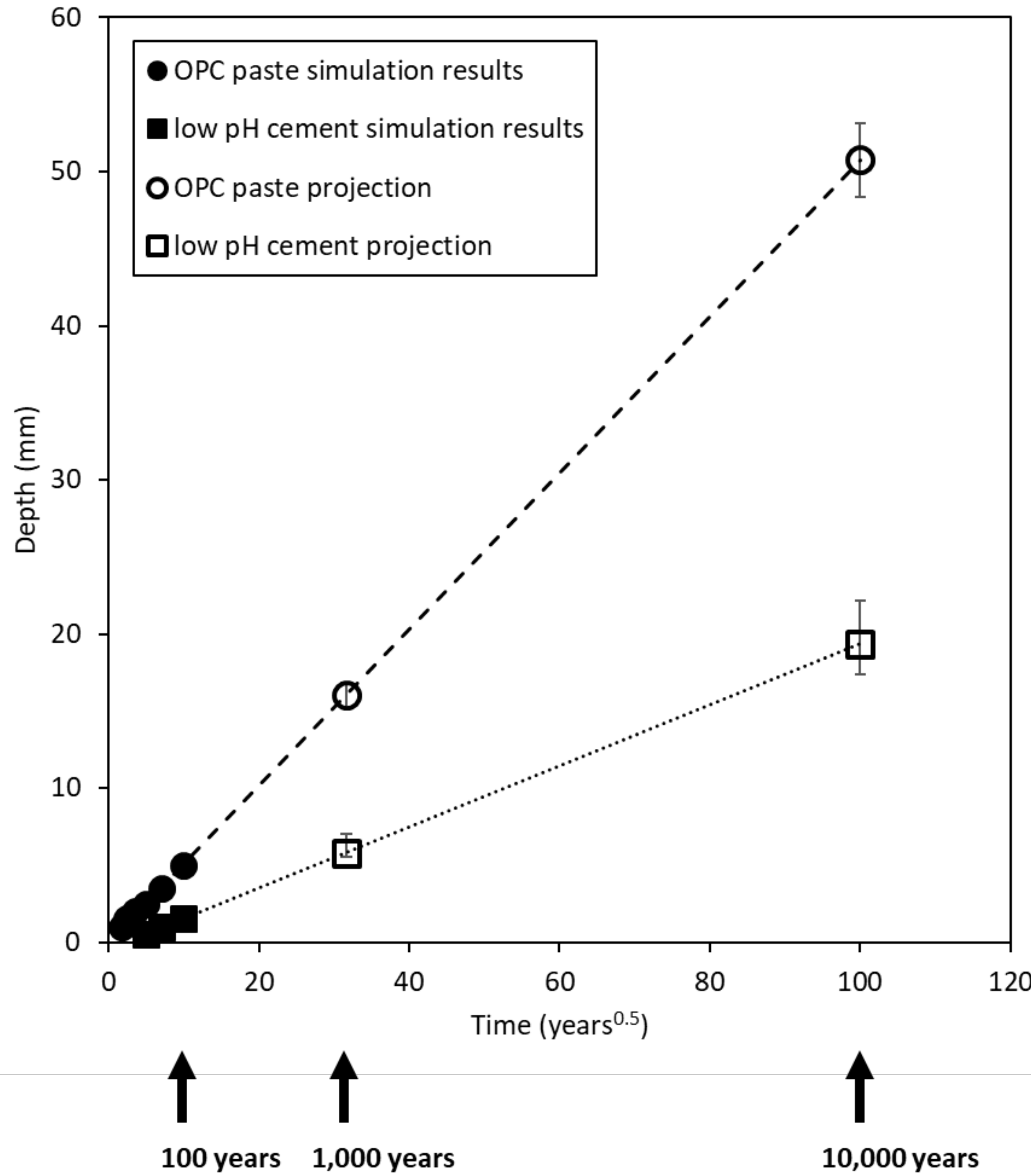
Oil shale – OPC paste:

- Complete CSH depletion near interface
- Portlandite depletion
- Ettringite formation
- Thaumsite formation (both sides of interface)

Oil shale - low pH cement:

- CSH depletion near interface
- Thaumsite formation
- Gypsum formation

Interface Models Results
Carbonation Front Progress Prediction



The location, X_C , of the moving carbonation front as a function of cement composition and conditions, when the relative humidity is above 50%, is (Papadakis et al., 1989):

$$X_c = A\sqrt{t}$$

X_c - the location, of the moving carbonation front (mm)

A - proportionality constant (mm $yr^{-0.5}$)

t - time (years)

Long-term scenarios (saturated conditions):

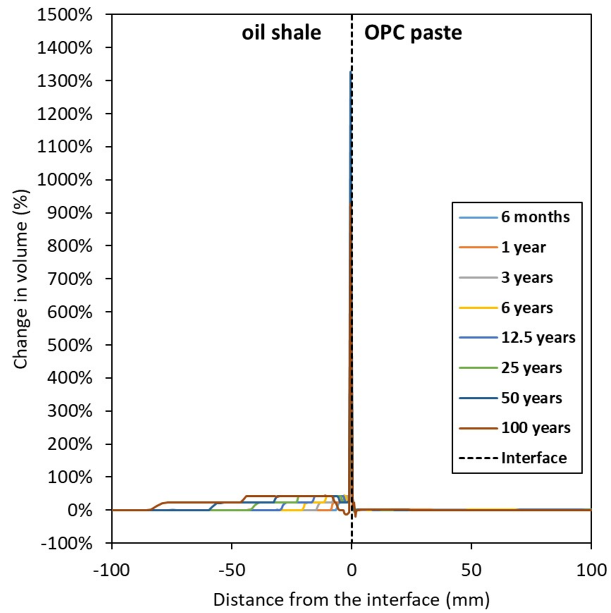
- **Oil shale-OPC: 16** and **51** mm of OPC are carbonated in 1,000 and 10,000 years
- **Oil shale-low pH cement: 6** and **19** mm of cement are carbonated in 1,000 and 10,000 years

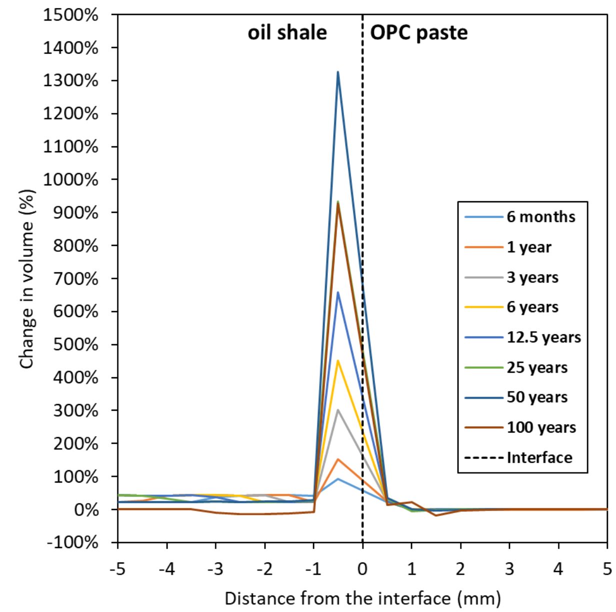
Estimates for the unsaturated case need to be addressed

Interface Models Results
Volume Change (≤ 100 yrs)

Oil shale – OPC paste

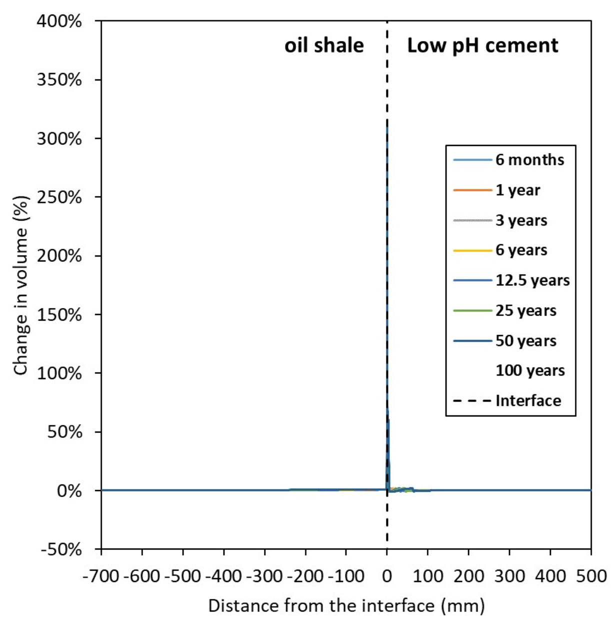
- Volume increase up to ~1300% ***in the rock***
- Most of the volume increase is thaumasite (334 cm^3/mol) formation with loss of calcite (37 cm^3/mol)

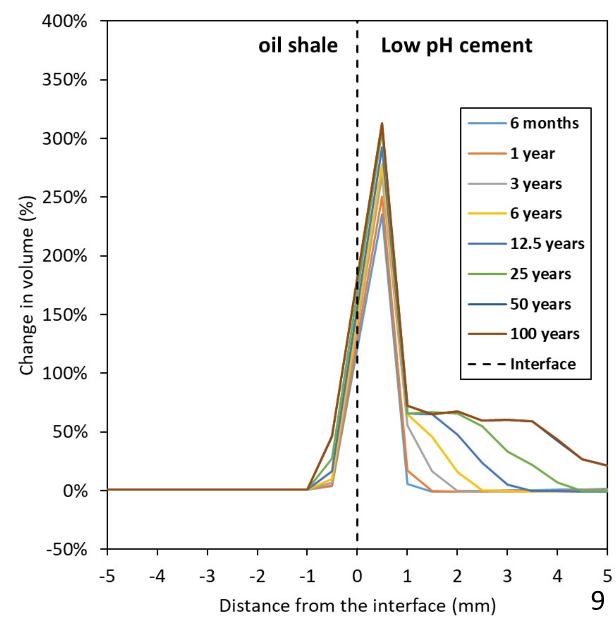




Oil shale – low pH cement

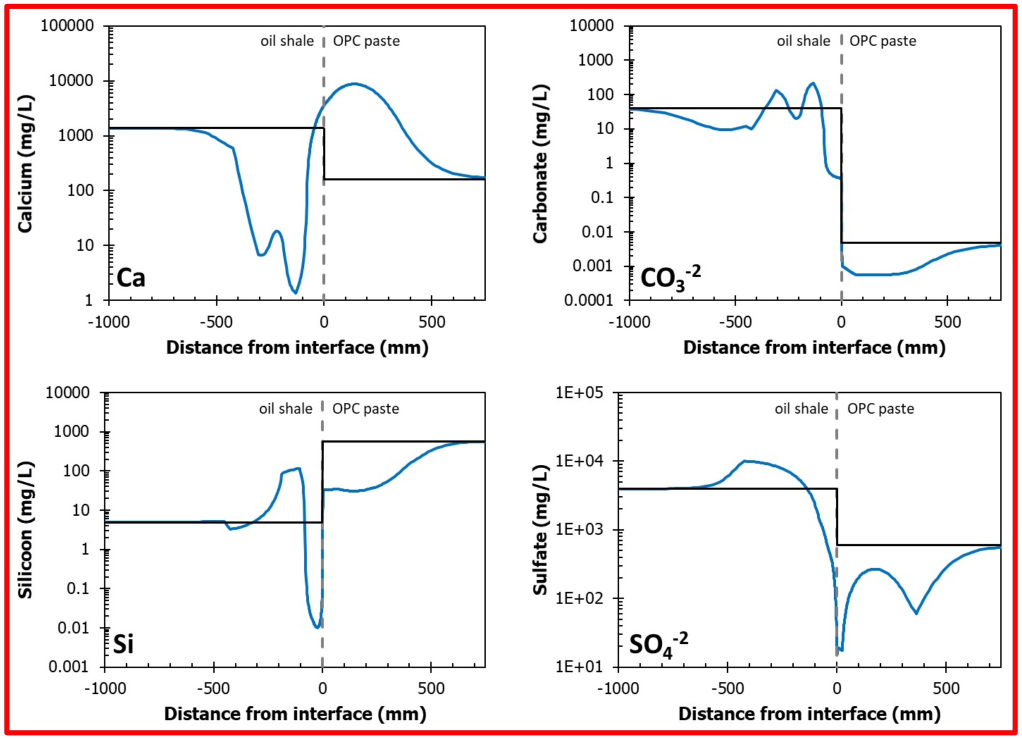
- Volume increase up to ~300% ***in the cement***
- Most of the volume increase is thaumasite (334 cm^3/mol) formation with loss of CSH (69 cm^3/mol)



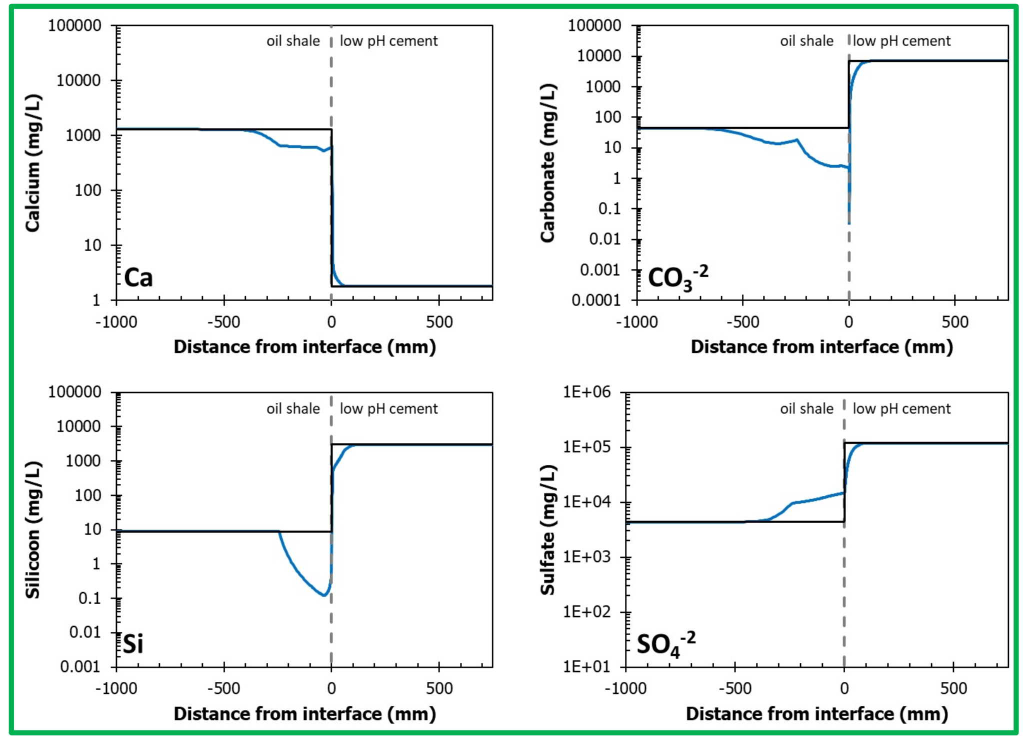


Interface Models Results
Majors Profiles

Oil shale – OPC paste



Oil shale – low pH cement



OPC paste vs. low pH cement:

- Diffusion distance in OPC paste is ~500 mm compared ~100 mm in low pH cement as a result of lower tortuosity factor (25 vs 75) and higher porosity (~25% vs ~16%)
- Significant change in oil shale pore water chemistry is observed deeper in the rock for OPC paste interface

Initial concentration
100 years
Interface

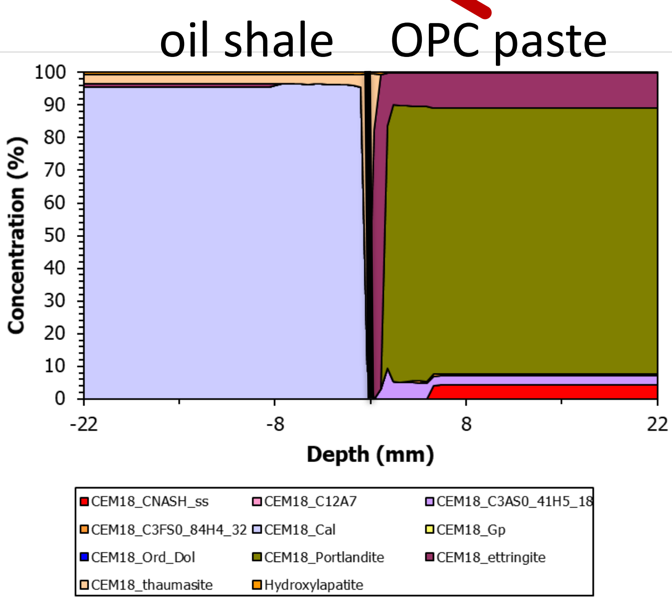
OPC paste Interfaces With Oil Shale/Marl/Limestone

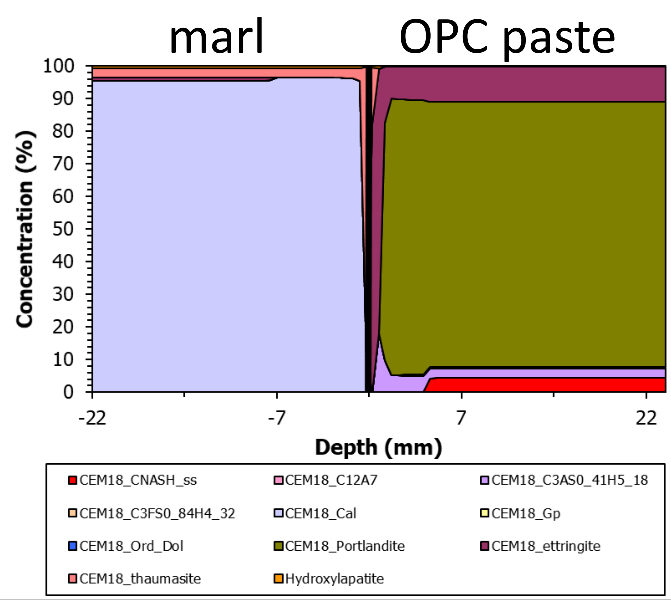
CO_3^{-2} (mol/L)	$7 \cdot 10^{-4}$
φ/τ^2	$4 \cdot 10^{-3}$

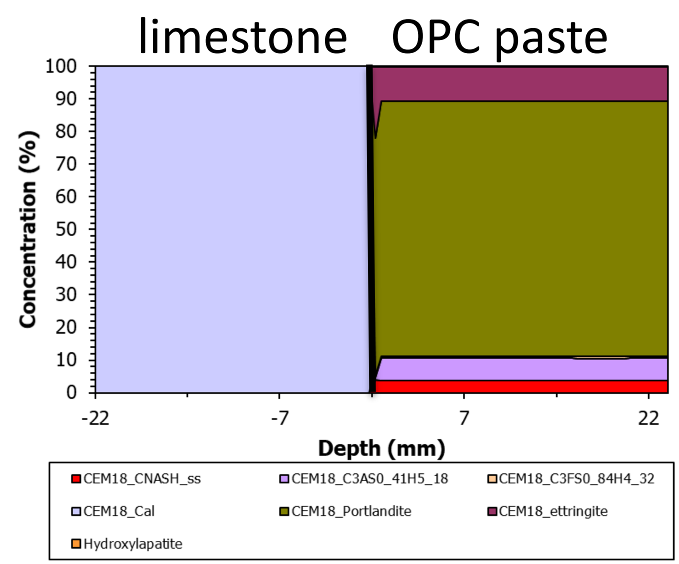
CO_3^{-2} (mol/L)	$3 \cdot 10^{-4}$
φ/τ^2	$9 \cdot 10^{-4}$

CO_3^{-2} (mol/L)	$7 \cdot 10^{-5}$
φ/τ^2	$7 \cdot 10^{-4}$

increasing reactivity ←







Key observations:

- Portlandite and CSH depletion in OPC paste
- Ettringite and Hydrogarnet formation in OPC paste
- Thaumasite formation in rocks (limestone and marl)

Depth of altered cement is controlled by porewater carbonate gradient and porosity/tortuosity² (φ/τ^2) ratio of the rocks

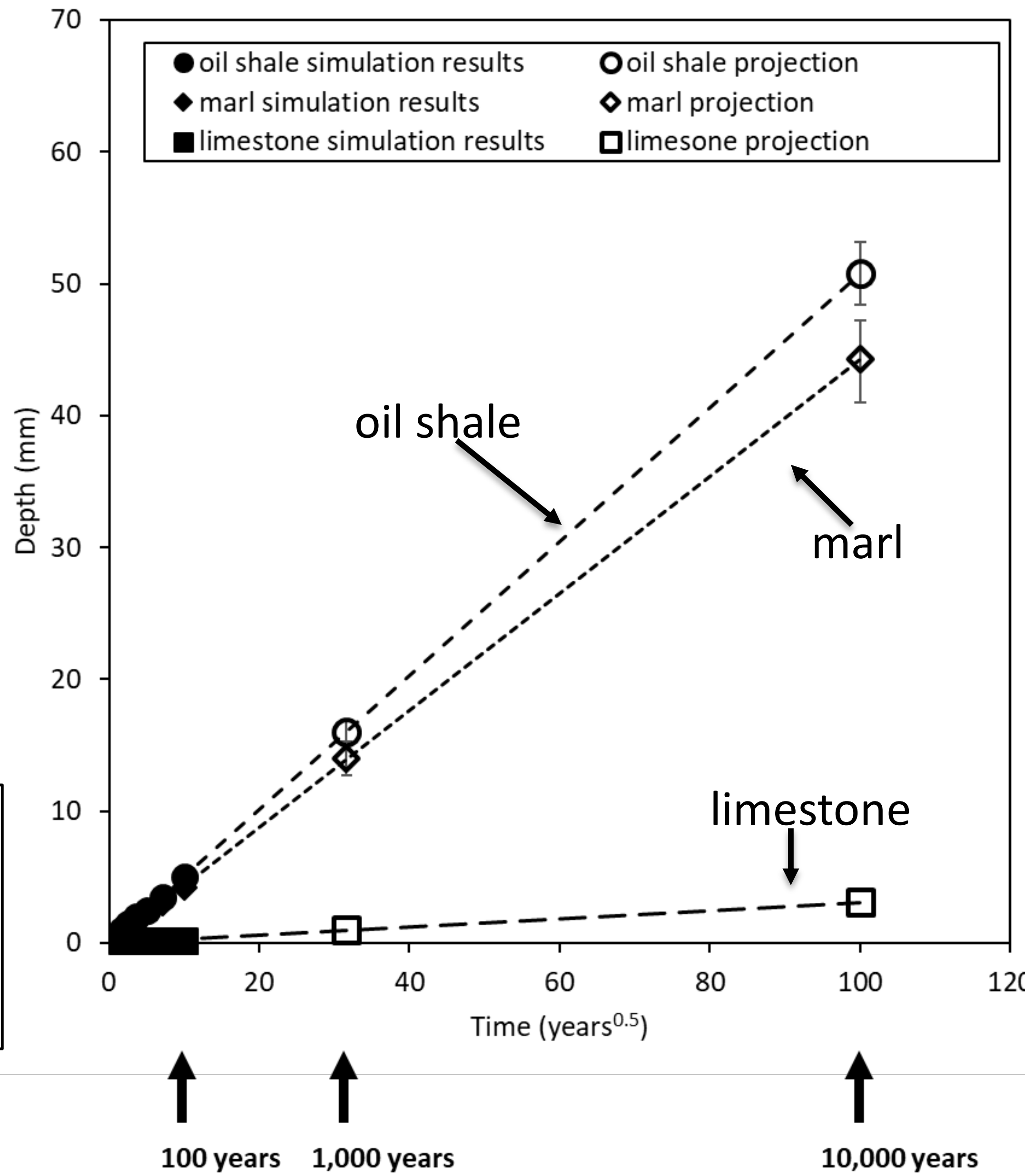
*CO_3^{-2} concentrations are dissolved porewater concentrations

OPC paste Interfaces With Oil Shale/Marl/Limestone

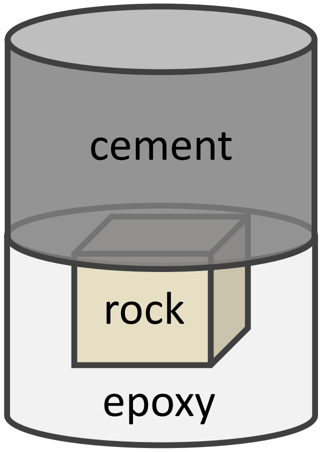
Long-term scenarios (saturated conditions):

- **Oil shale-OPC: ~16** and **~51** mm of OPC are carbonated in 1,000 and 10,000 years
- **Marl-low pH cement: ~14** and **~43** mm of cement are carbonated in 1,000 and 10,000 years
- **Limestone-low pH cement: ~1** and **~4** mm of cement are carbonated in 1,000 and 10,000 years

Based on simulations results a better host rock will be a rock with **low carbonate concentration** in pore water and **high porosity/tortuosity² (φ/τ^2)**



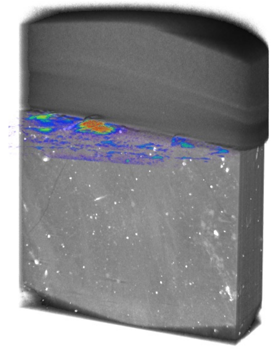
Experimental Project Approach



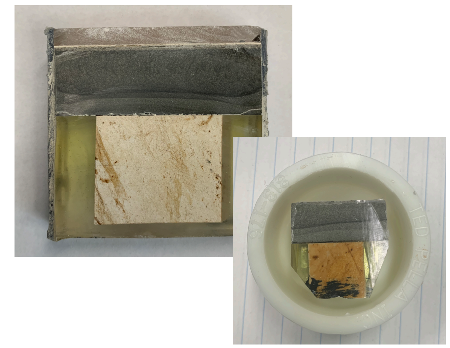
Aging

1-3 yr

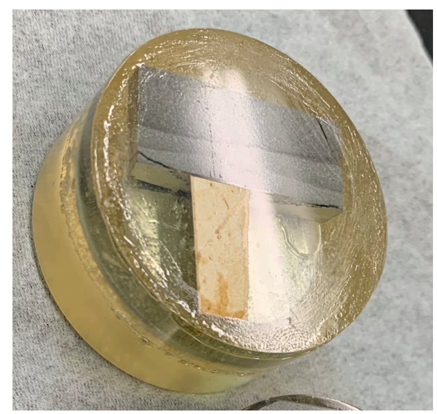
MicroCT



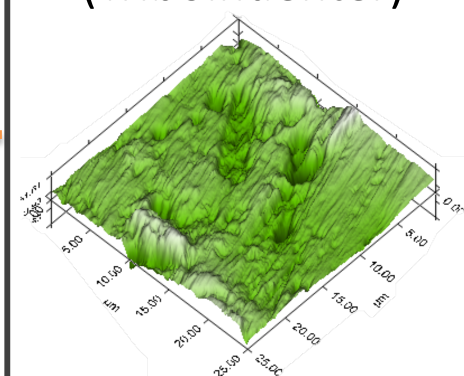
Sectioning



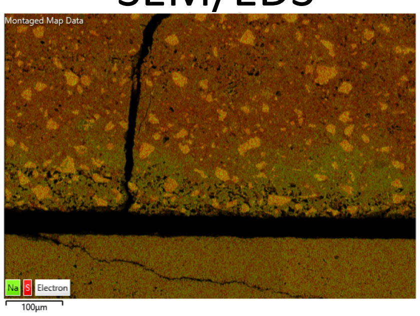
Polishing



Surface Roughness (Triboindenter)



SEM/EDS



Micro/Nanoindentation & Fiducial Placement

micro – rocks + cement

nano – cement

LA-ICP-MS

image co-registration with SEM/EDS

laser depth & concentration profiling

One-Dimensional Reactive Transport Modeling with PFLOTRAN: Marl Leaching*

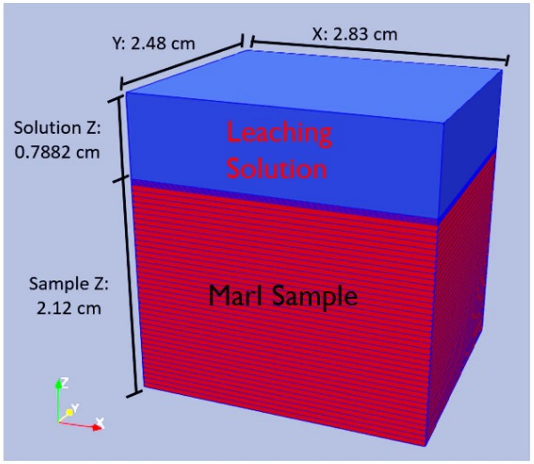
Carlos F. Jove Colon, Carlos M. Lopez, Kris Kuhlman, Ed Matteo (SNL)

Objective: To represent a leaching experiment (EPA Method 1315) of a marl rock sample with a 1D reactive transport model using PFLOTRAN** that captures episodic changes of solution chemistries at leaching intervals.

Problem Setup:

- Mesh discretization: One cell for the leaching/bath solution (top); 43 cells for the solid monolith (bottom)
- Marl porosity (~32%), estimated from constituent mineral fractions (XRD)
- Darcy permeability = 10^{-16} m^2
- Marl minerals (vol. fractions):
  - Calcite (0.64) – Constrained from XRD
  - Kaolinite (0.021)) – Constrained from XRD
  - Quartz (7 × 10-3)) – Constrained from XRD
  - Halite (7.5 × 10-4) – From fitting experimental [Na+] profile
  - Sylvite (2.7 × 10-5) – From fitting experimental [K+] profile
  - Other phases allowed to form
- Small pressure perturbations in leaching solution cell (top): Resulted in minor effects to the solute concentration profiles

Experimental Sample Setup



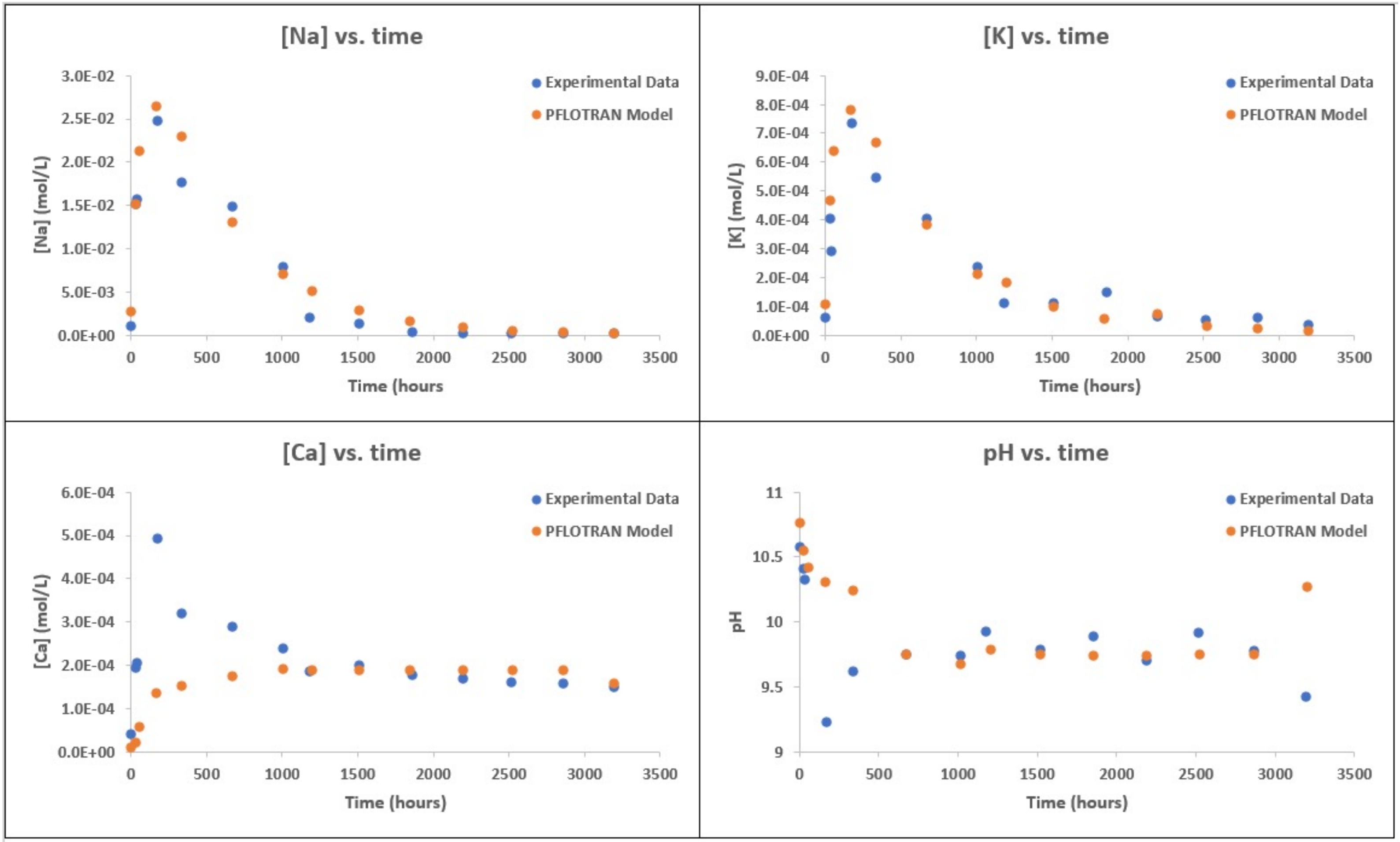
Sample Meshed Domain

* Jove Colon et al (2021). Evaluation of nuclear spent fuel disposal in clay-bearing rock-process model development and experimental studies. Sandia National Labs (SNL), Albuquerque, NM (United States). SAND2021-13578 R

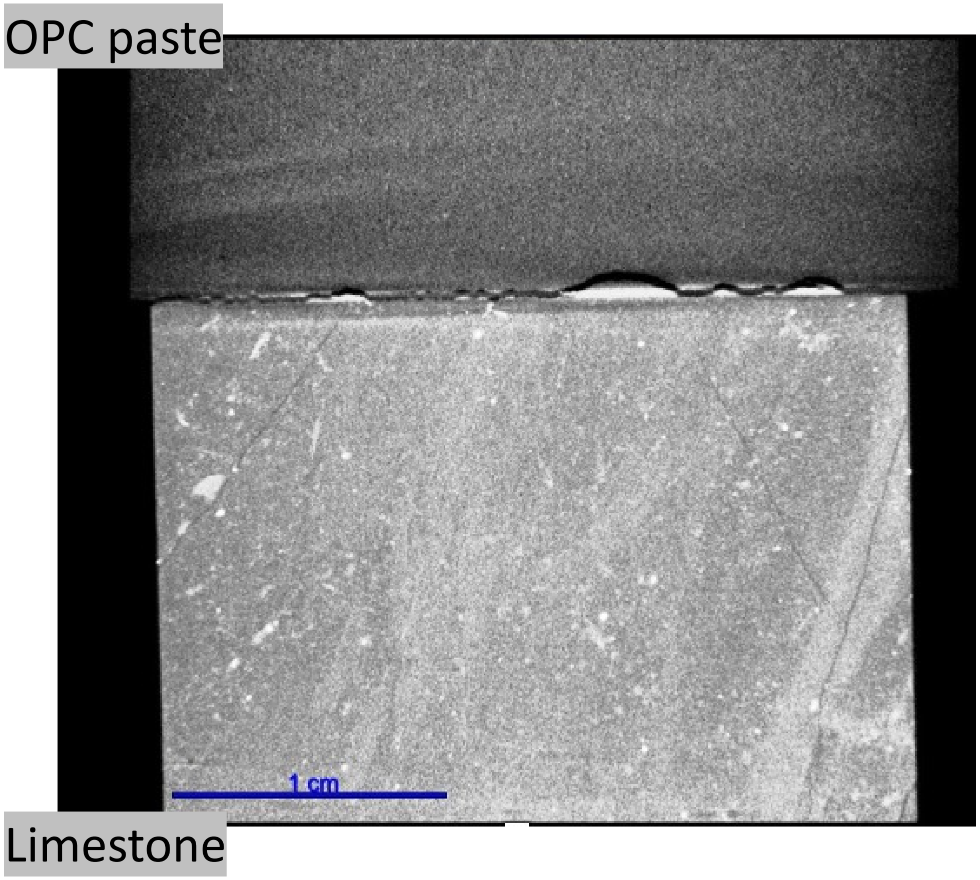
** Lichtner, P.C., Hammond, G.E., et al. (2019). PFLOTRAN user manual: A massively parallel reactive flow and transport model for describing surface and subsurface processes. Los Alamos National Lab. (LANL), Los Alamos, NM (United States); http://documentation.pflotran.org.

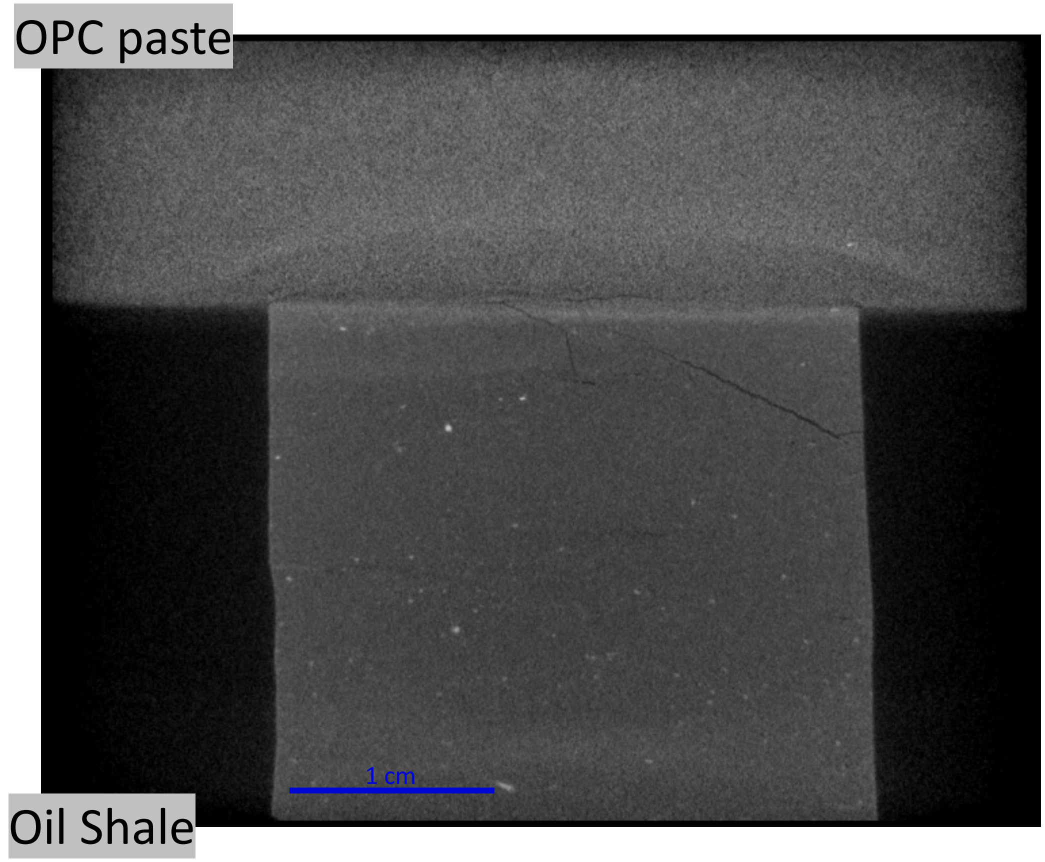
Preliminary Results: [Na], [K], [Ca], pH vs. time profiles

- The overall temporal [Na^+] and [K^+] profiles are well represented by using halite (NaCl) & sylvite (KCl) as reactant phases in marl.
- Both profiles were used to constrain a diffusion coefficient value to 2.5×10^{-10} cm^2/s.
- Some discrepancies in [Ca] and pH predictions with experiments at early times. Closer agreement is attained at later times.



MicroCT



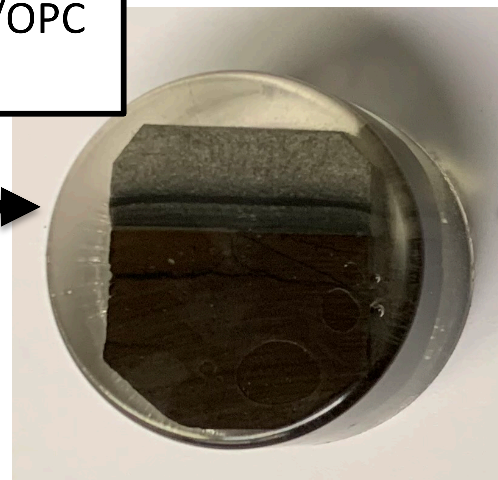


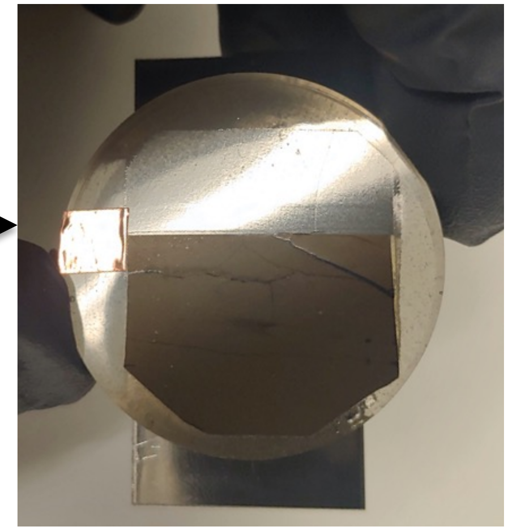
- Provides information about contact area and void volume at interface
- Helps identify features of interest and precise locations for sectioning and characterization

Sample Preparation

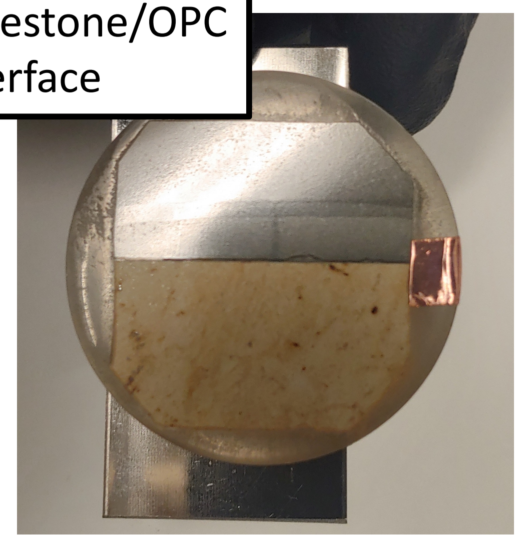
GOAL: average surface roughness of 50 nm, measured using scanning probe microscopy (SPM)

doped oil shale/OPC interface



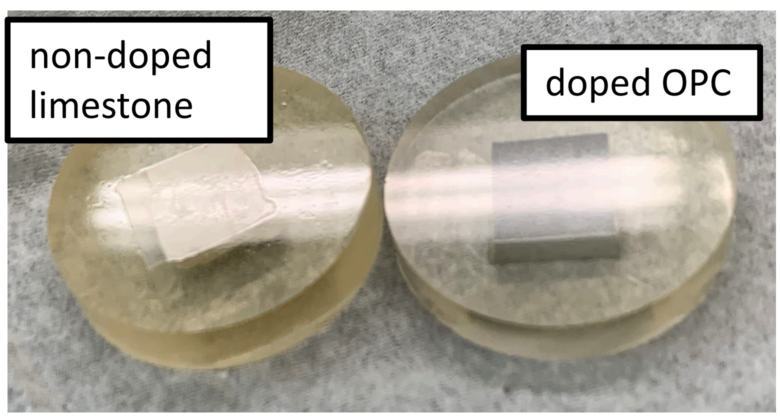


doped limestone/OPC interface

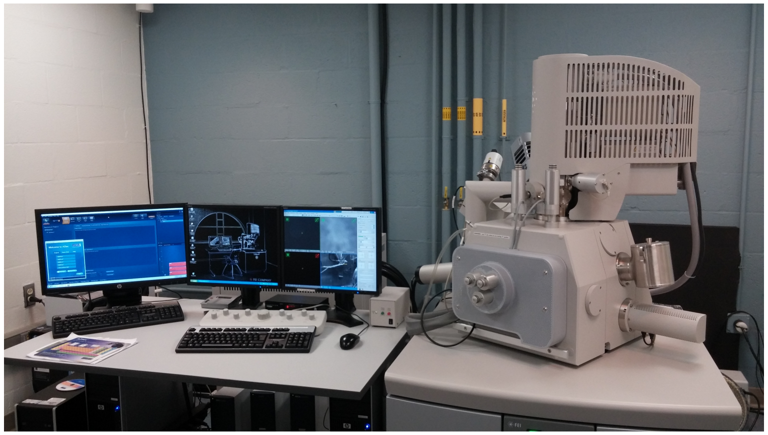


Challenges:

- two materials polish at different rates, so minimizing sample size and hard edges is necessary
- dopants reduce polish ability of the rocks



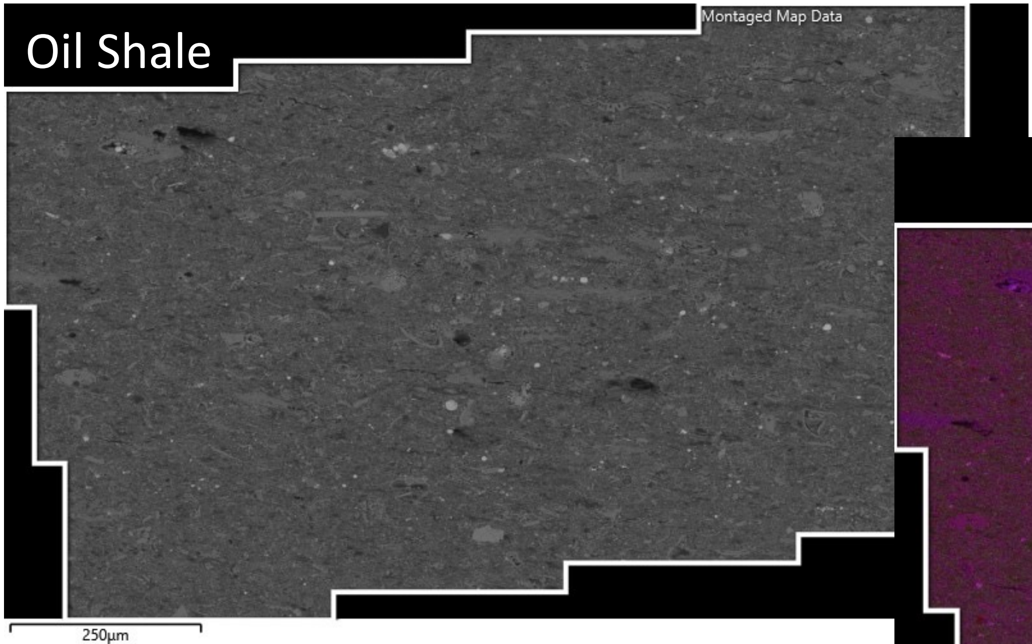
SEM/EDS

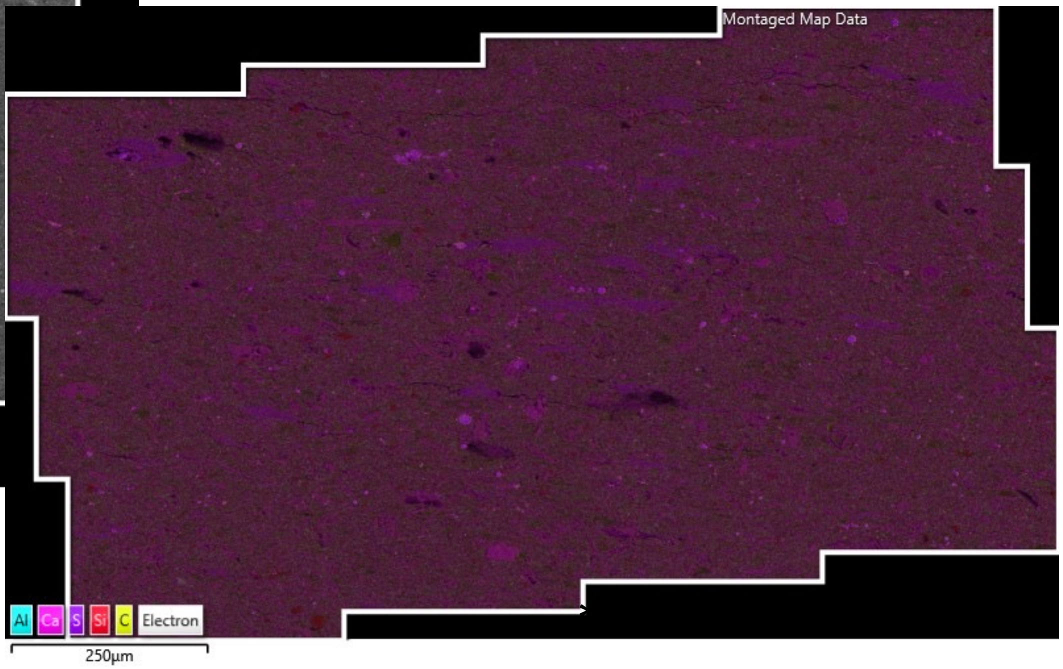


- Large area mapping utilized to investigate microstructure, morphology, and chemistry (major elemental concentrations)

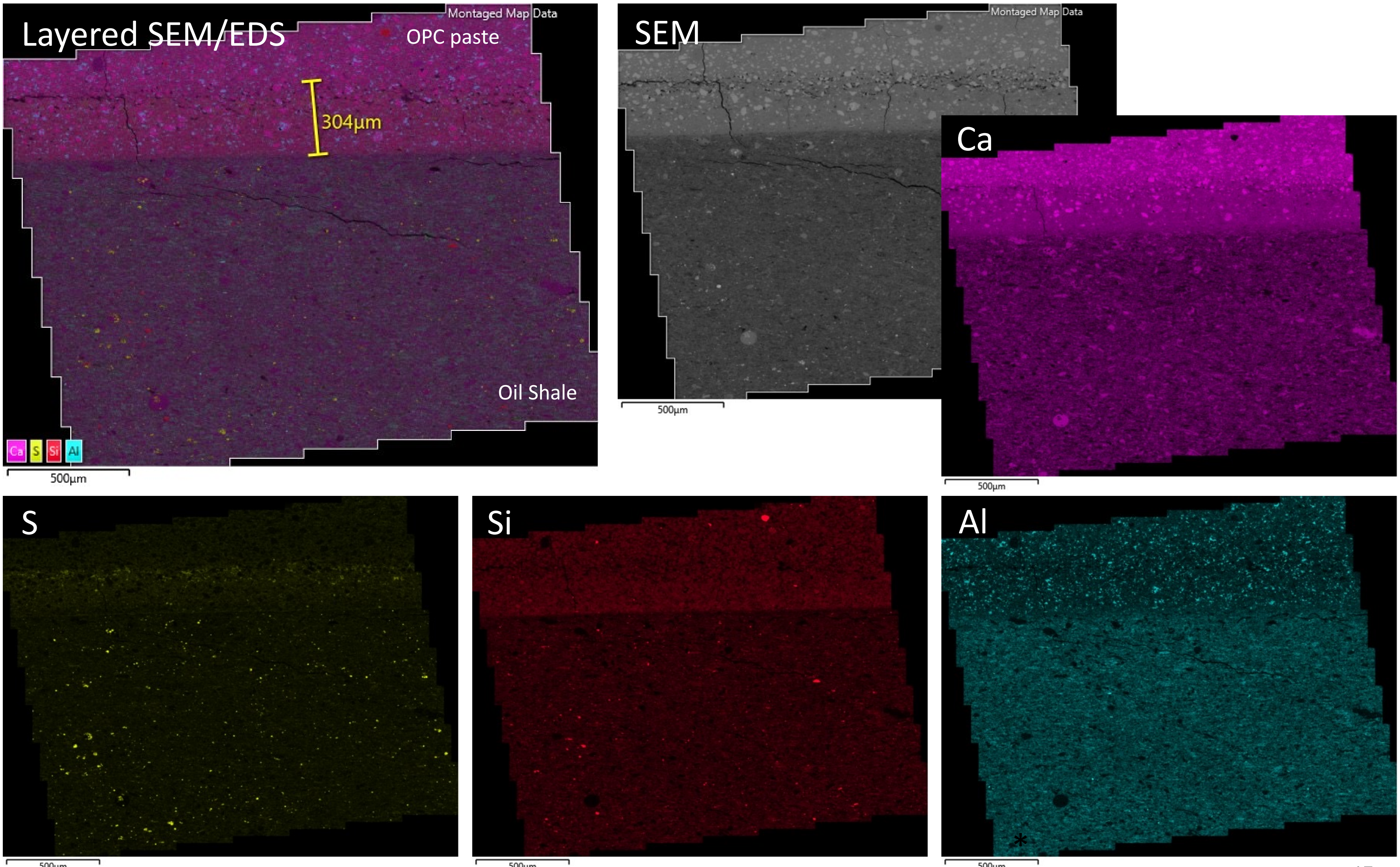
ESEM imaging conditions:
15kV, spot size 3.5, 130 Pa, 600x, pixel dwell time 30µs, resolution 1024x874

EDS collection conditions:
pixel dwell time 30µs, frame count 20, process time 5, resolution 1024x874



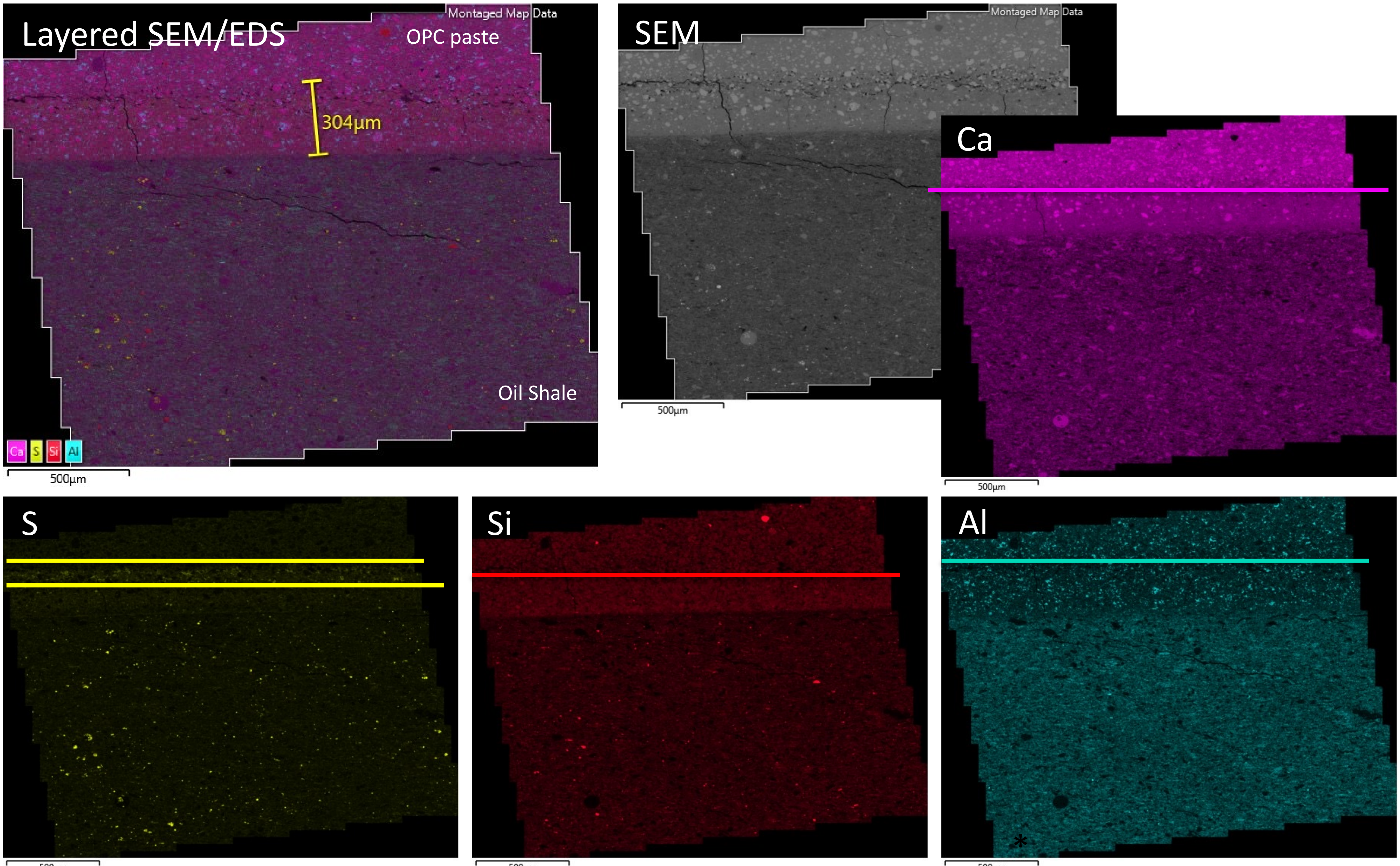


SEM/EDS

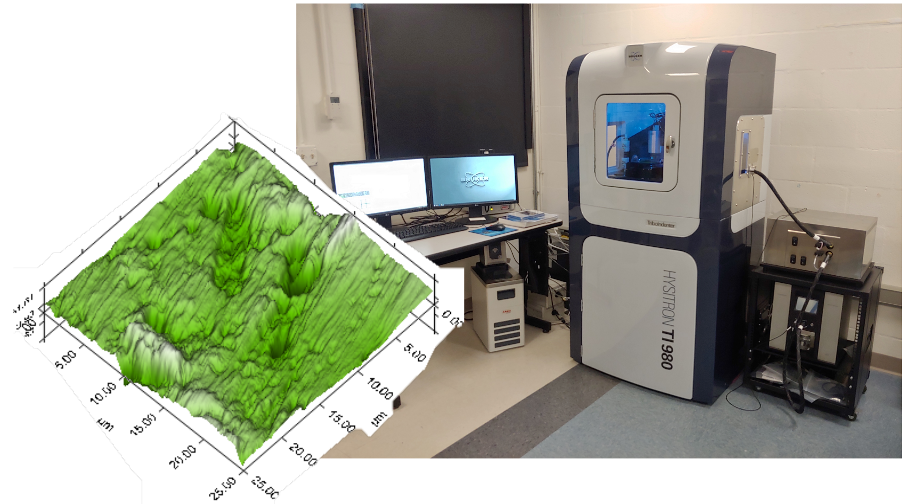


Layered SEM/EDS
Montaged Map Data
OPC paste
304µm
Oil Shale
Ca
S
Si
Al
500µm
SEM
Montaged Map Data
500µm
Ca
500µm
S
500µm
Si
500µm
Al
500µm

SEM/EDS


Layered SEM/EDS
Montaged Map Data
OPC paste
304µm
Oil Shale
Ca
S
Si
Al
500µm
SEM
Montaged Map Data
500µm
Ca
500µm
S
500µm
Si
500µm
Al
500µm

Nano and Micromechanical Testing



Scanning Probe Microscopy (SPM)

- Provides verification of surface roughness prior to indentation
- Used to map sample surface features

Microindentation

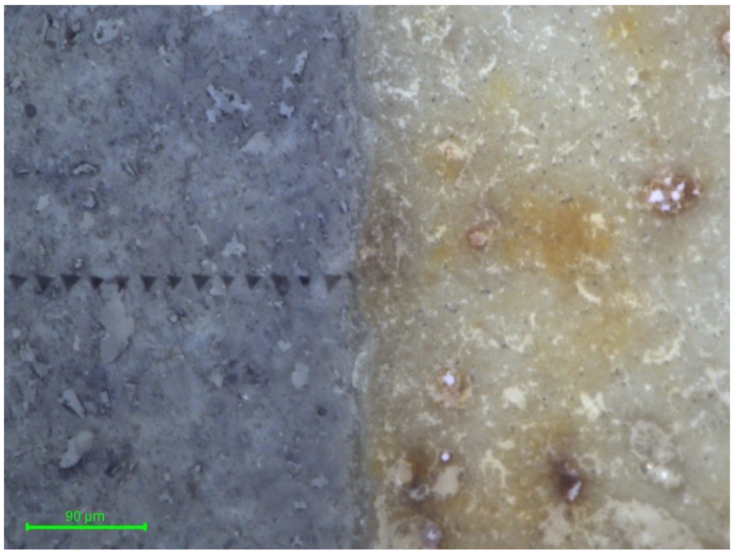
- Investigate mechanical properties across interfaces and as a function of sample depth

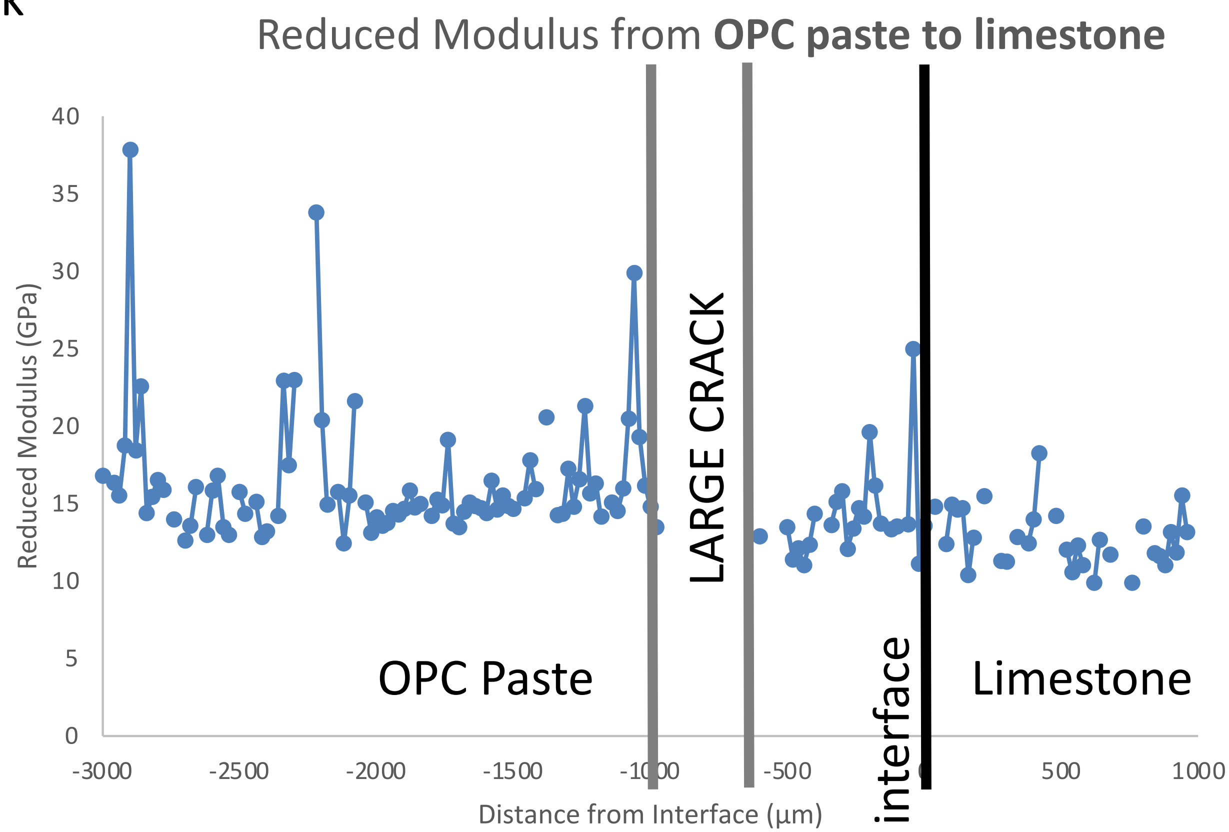
Nanoindentation

- Accelerated Property Mapping (XPM) to investigate hardness and modulus in close proximity to interfaces
- Analyze cement phase distribution [upcoming]
  - limited to cement due to dopant influence on rock's ability to polish
  - phase deconvolution will help understand impact of trace constituents

Microindentation

- More indents in cement than rock to capture potential mechanical gradients



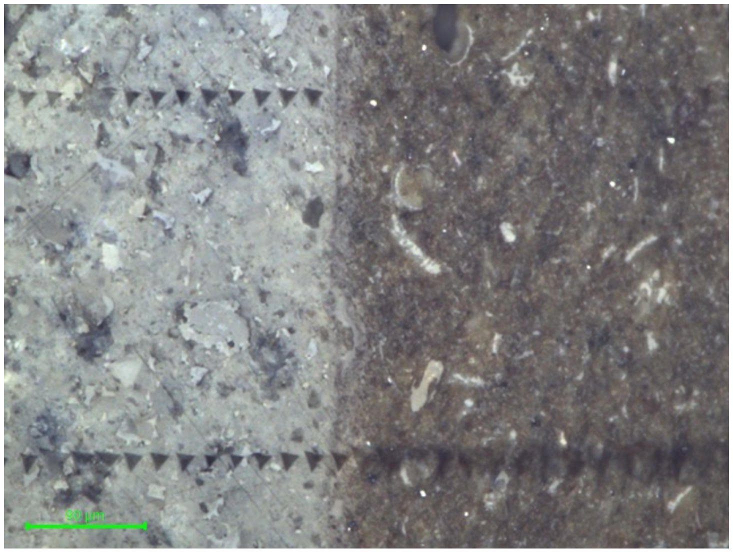


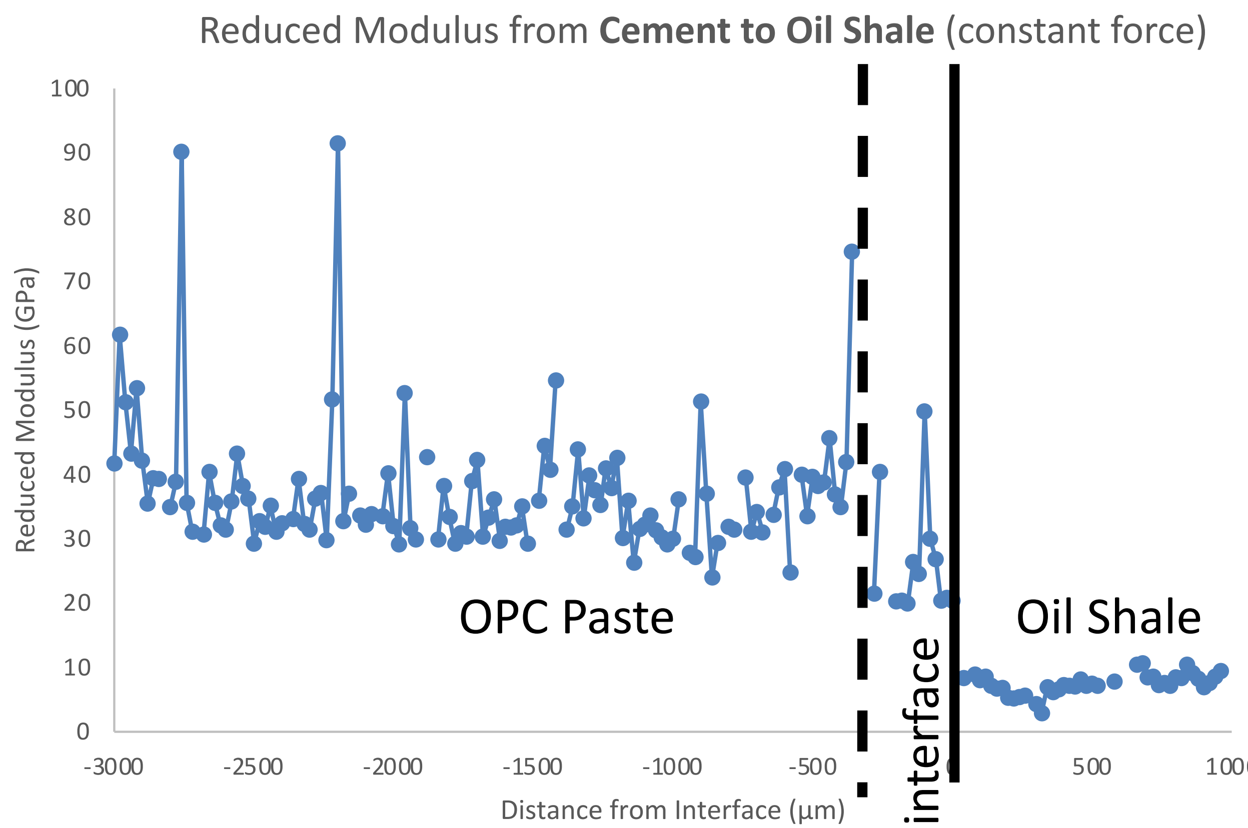
Triboindenter Conditions

Berkovich tip
peak load 75 mN
10-15-10 sec – trapezoidal load function

- No defined mechanical changes observed at the interface between OPC paste and limestone

Microindentation





Triboindenter Conditions

Berkovich tip
peak load 75 mN
10-15-10 sec – trapezoidal load function

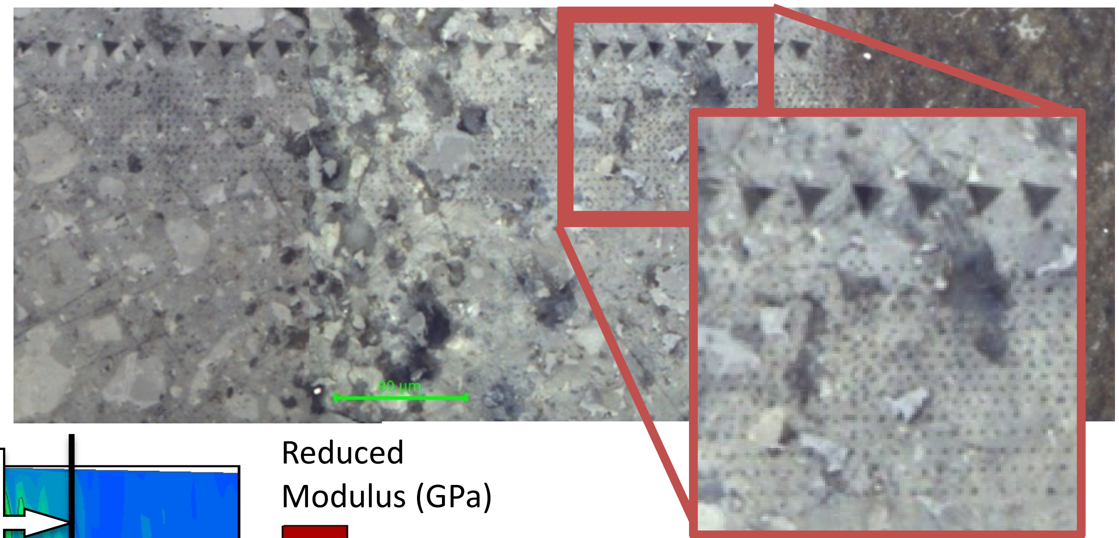
- Within 300 µm of the interface there is a 30% reduction in average moduli of the OPC paste

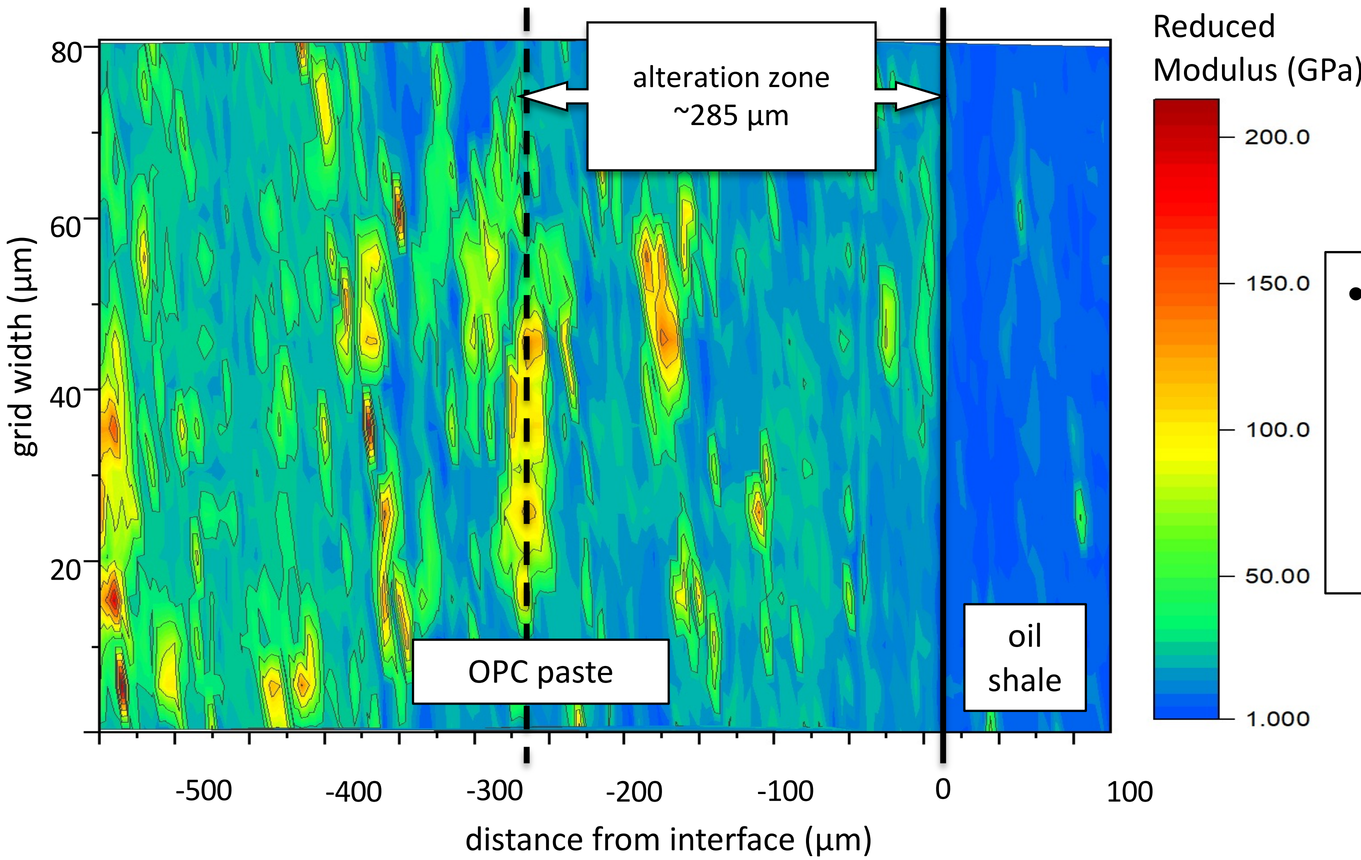
Accelerated Property Mapping (XPM)

- **Series of square grids (85 x 85 μm) crossing over interface region**

Triboindenter Conditions

Berkovich tip
peak load 2 mN
3-5-3 sec – trapezoidal load function





- Nanoscale tip shows gradually reducing modulus values in a nearly identical alteration zone as the micro-indentation data

From Simulations → Experiments

AFTER 1 YEAR OF EXPOSURE:

OPC-Oil Shale Interface

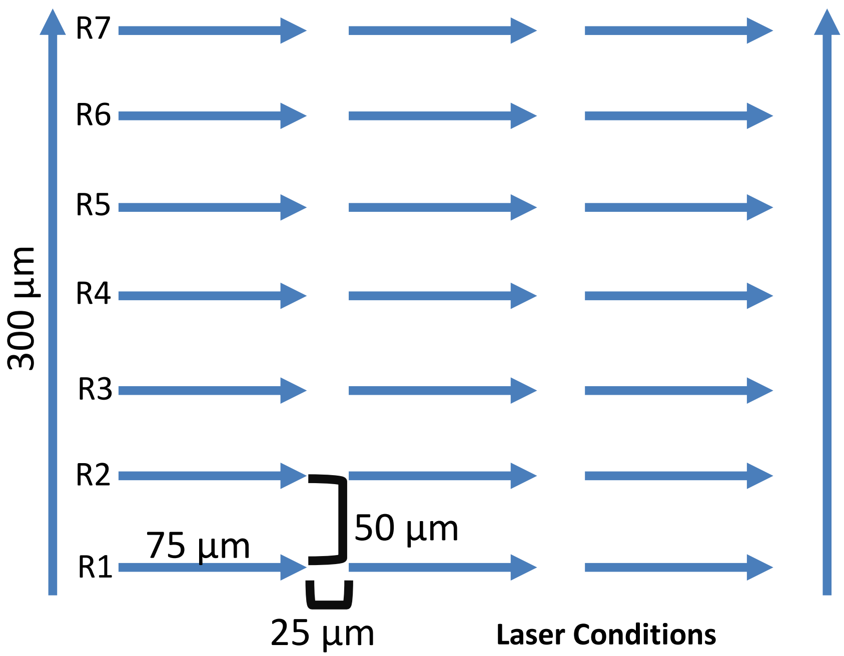
- **Simulation results:** an alteration zone of 500 μm is estimated
- **Laboratory experiments, chemical data:** elemental gradients in Ca, Si, Al, and S in the OPC paste form an alteration zone of ~300 μm
- **Laboratory experiments, mechanical data:** suggests reduced moduli values in OPC paste at a depth of 300 μm ± 20 μm from the interface

OPC-Limestone Interface

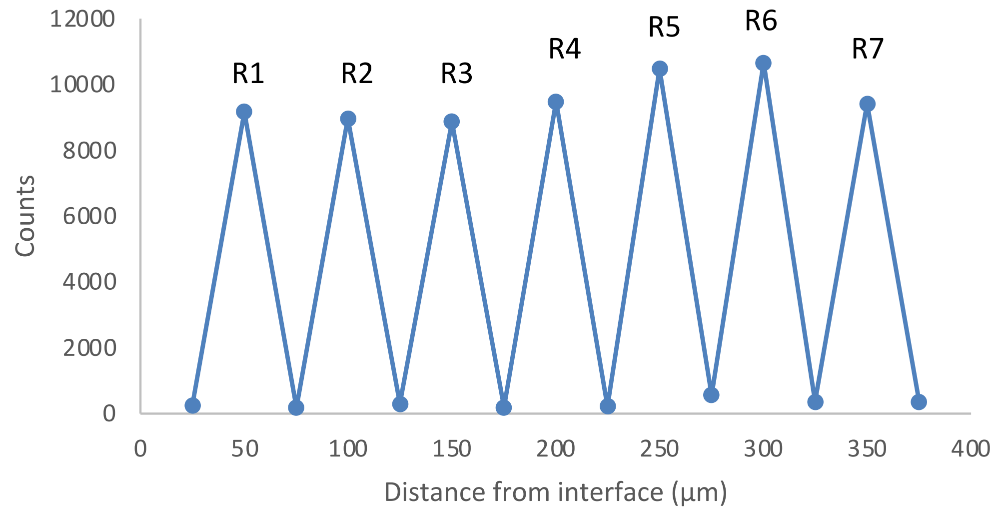
- Experiments confirm simulation data showing no chemical or mechanical alteration zone

Oil shale – OPC paste interface		
SEM-EDS (elemental gradients)	Microindentation/XPM (reduced moduli)	Simulation results
300 μm	300 μm	500 μm

Laser Ablation –
Preliminary Results: Limestone-OPC Interface



Ca43 - moving away from interface



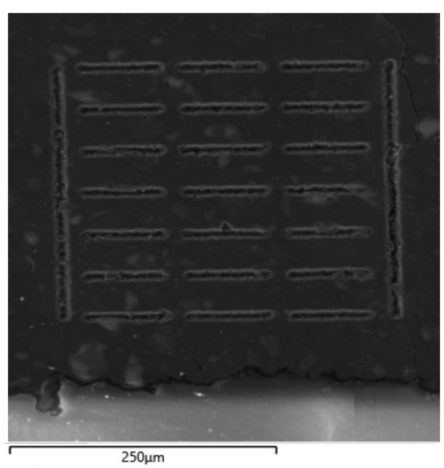
Laser Conditions

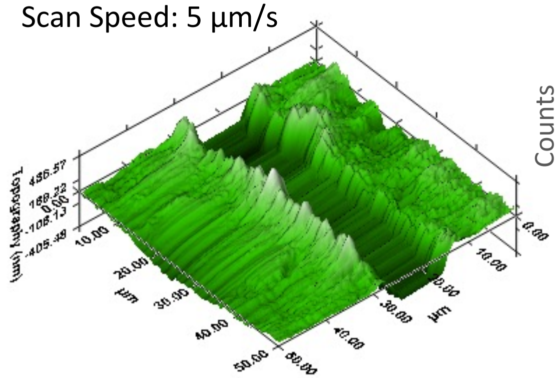
Energy: 7 J/cm^2

Frequency: 4 Hz

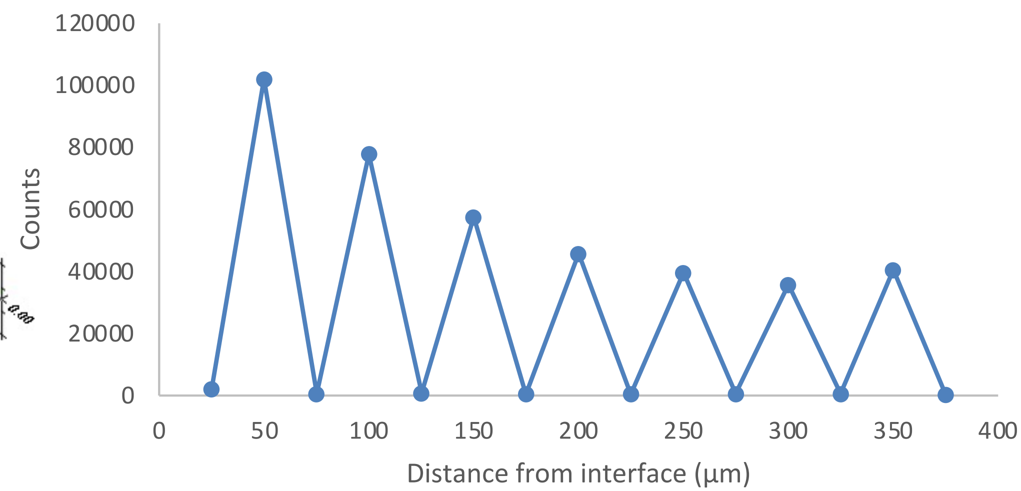
Spot Size: 10 µm

Scan Speed: 5 µm/s





U238 - moving away from interface



Future Directions

Experimental:

- Currently in advanced stages of designing approach to laser ablation measurements
  - provides quantitation of the dopant concentrations as a function of distance from the interface
- Perform grid nanoindentation and analyze data to get mechanical information on the cementitious phases through the alteration zone
- Complete characterization of aged low pH cement interfaces for comparison to OPC pastes

Modeling:

- Rock-cement interface simulations with dopants (Li, Ce, Cr and U)
- Simulations of unsaturated conditions and moisture transport

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