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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***

Completed

measured

Data from
cement/rock
interface
experiments

planning

Cement/rock
interface
modeling -
prediction

Interface Evaluations

- 6 rock types, each with 2 cements
- Experiments – ca. 1-2 years
- Simulations

Experimental planning

Experimental data interpretation

Long-term prediction

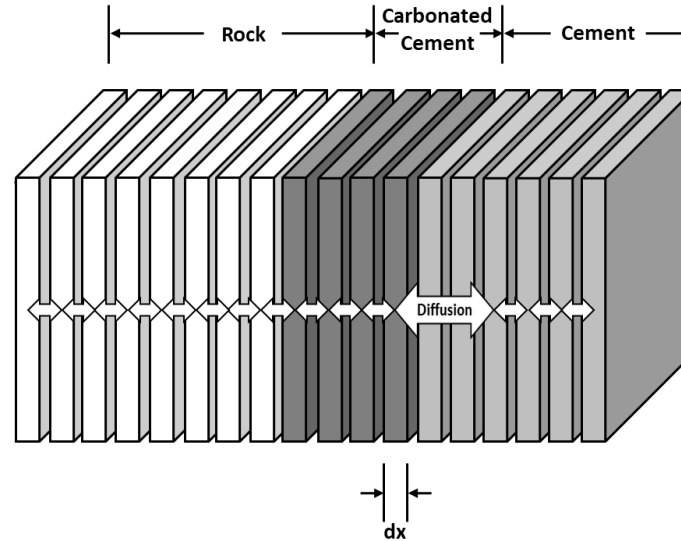
measured

comparison

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



Conceptual Model – Rock/Cement Interface



Model assumptions:

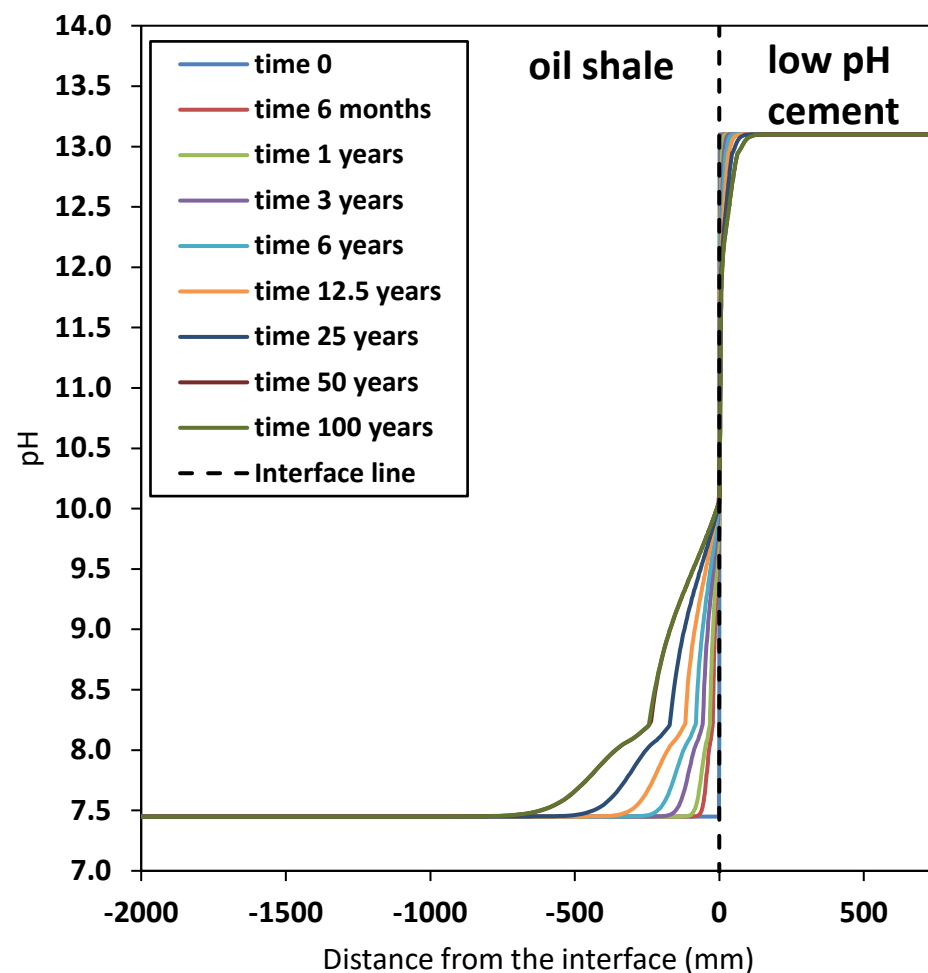
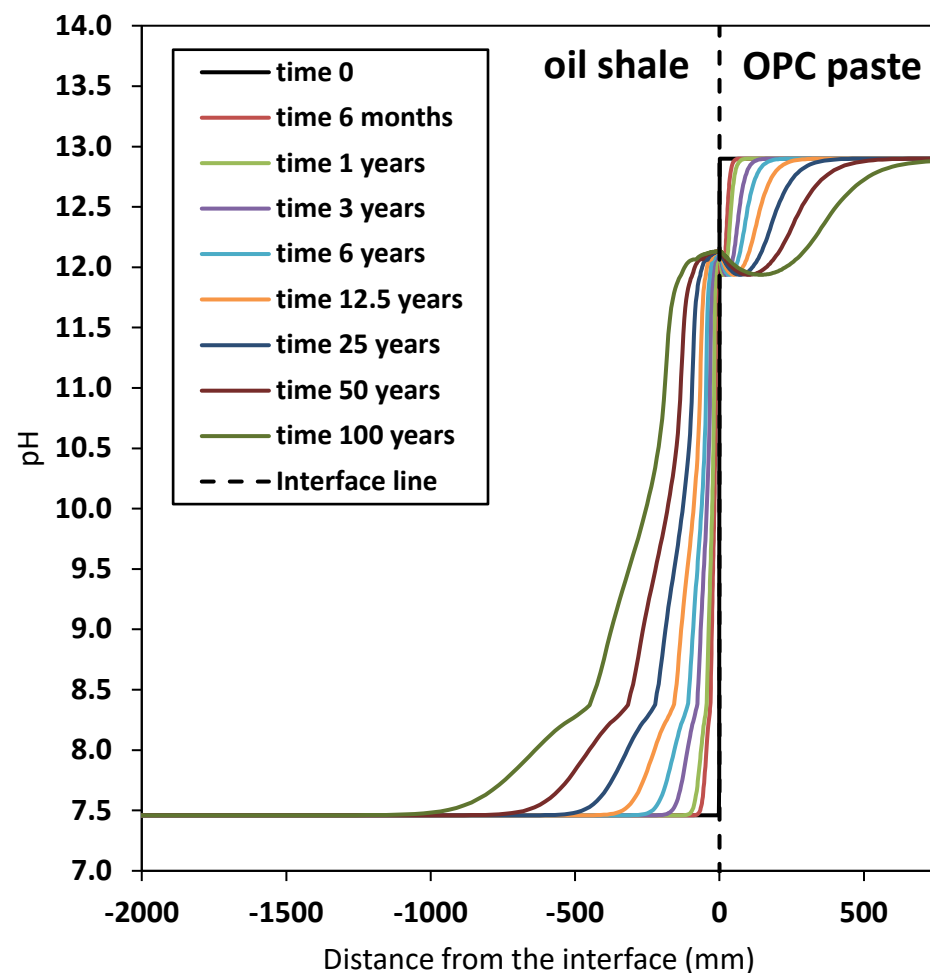
1. Each cell is well mixed
2. Local equilibrium
3. C-(N-)A-S-H solid solutions
4. Multi-ionic diffusion only
5. Materials intact throughout the entire simulation

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

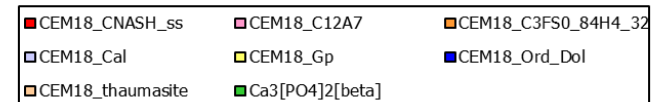
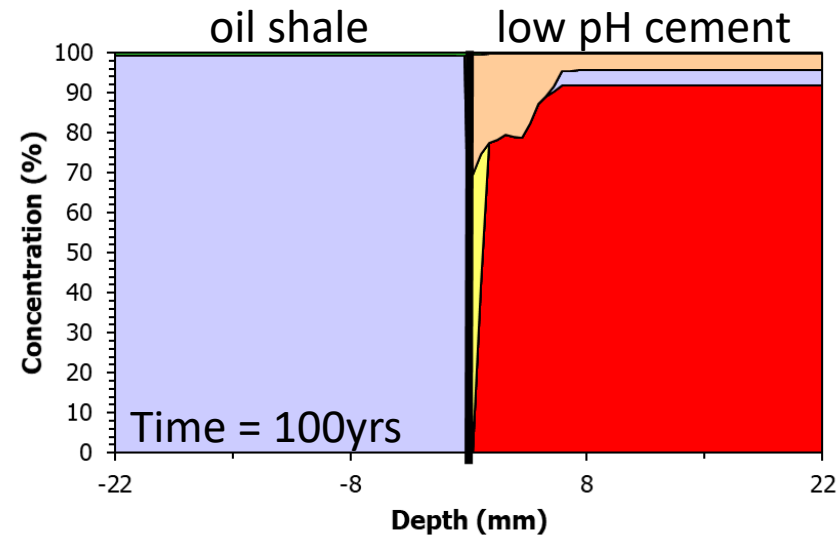
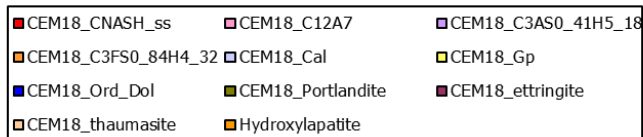
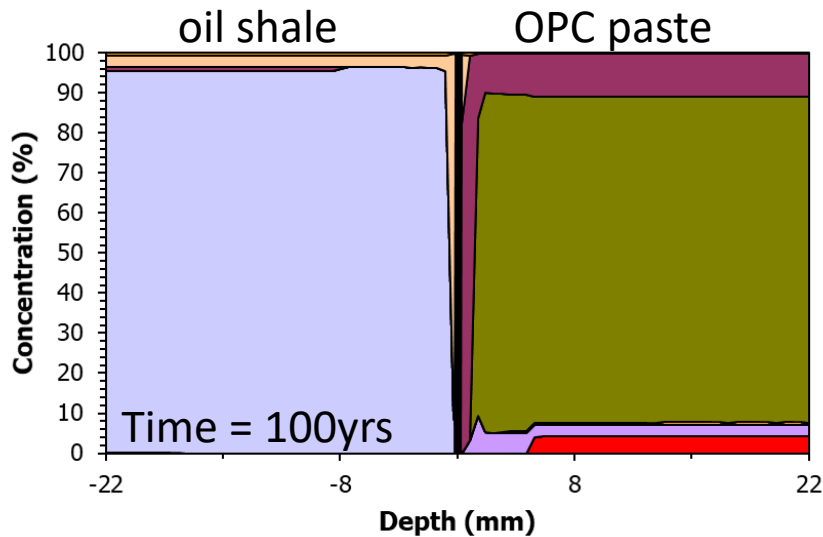


Simulations Results – pH Profiles





Simulation Results (100 yrs) – Solid Phases Distribution Profiles



Oil shale – OPC paste:

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

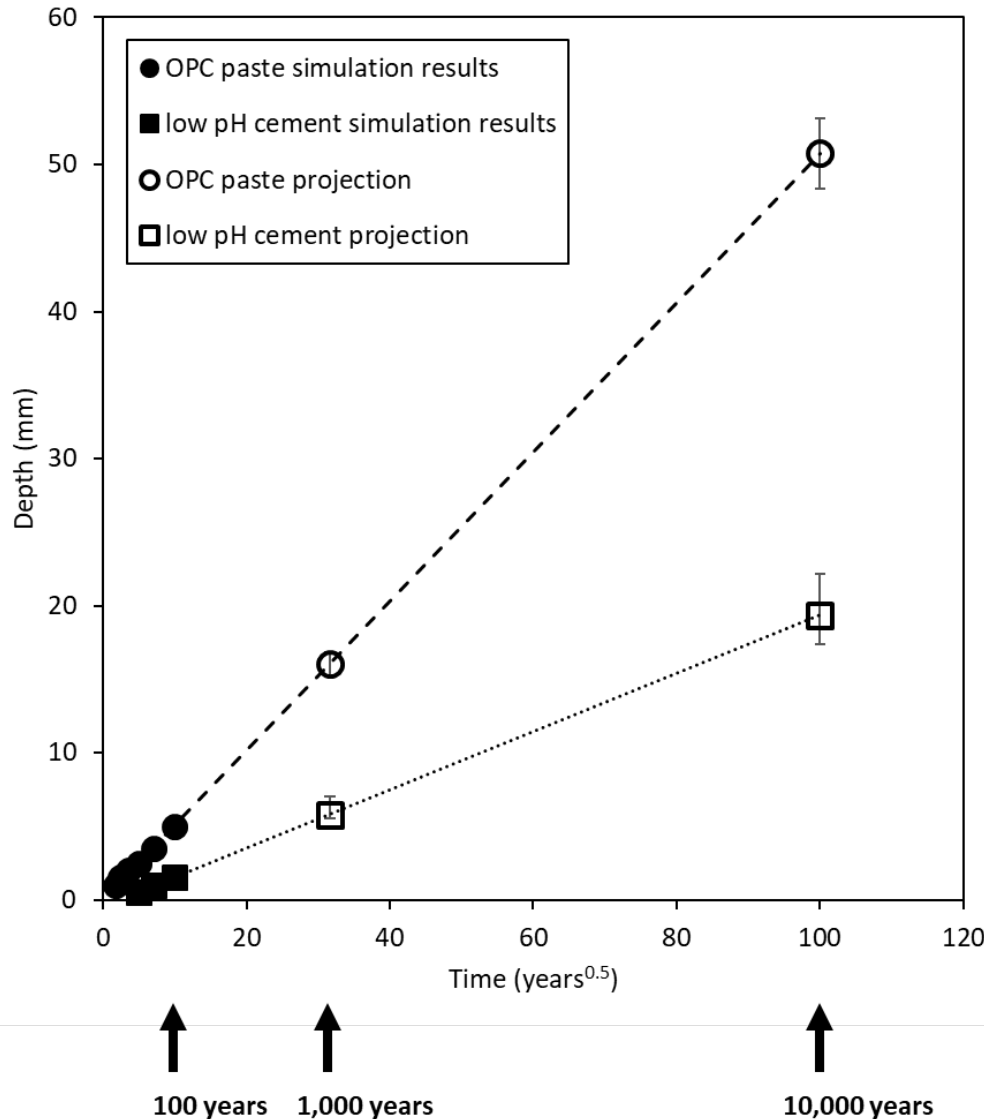
Oil shale - low pH cement:

- CSH depletion near interface
- Thaumasite 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

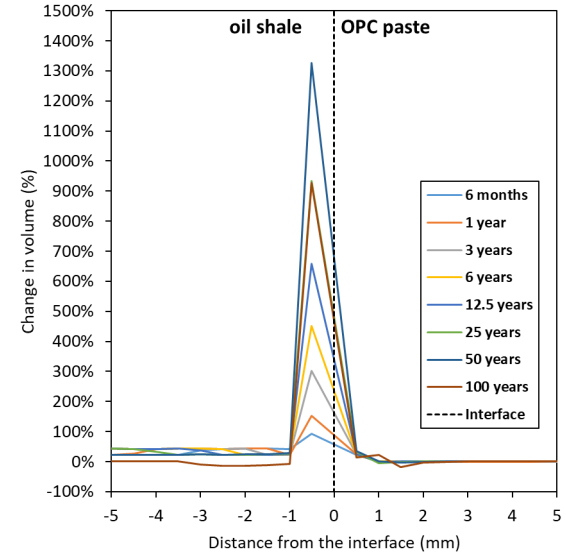
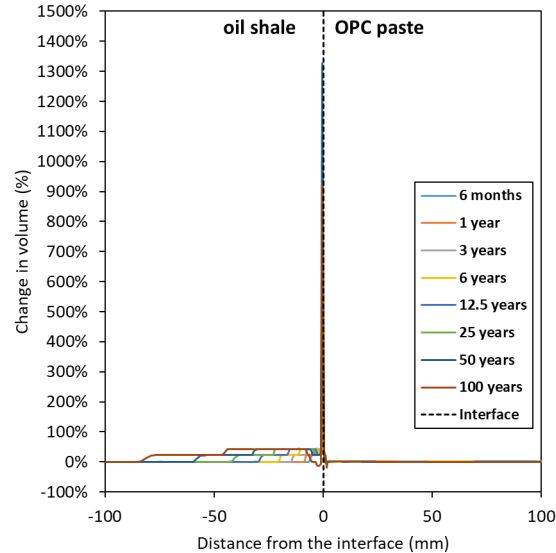


Interface Models Results

Volume Change (≤ 100 yrs)

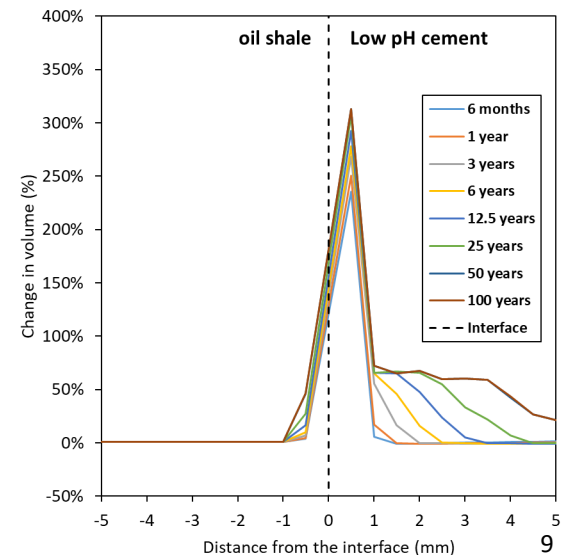
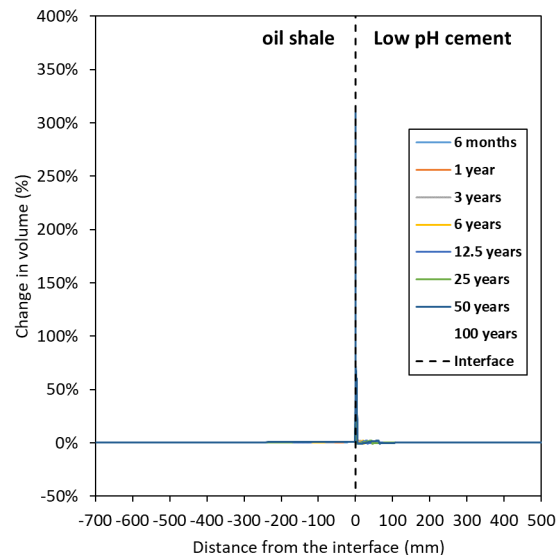
Oil shale – OPC paste

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



Oil shale – low pH cement

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

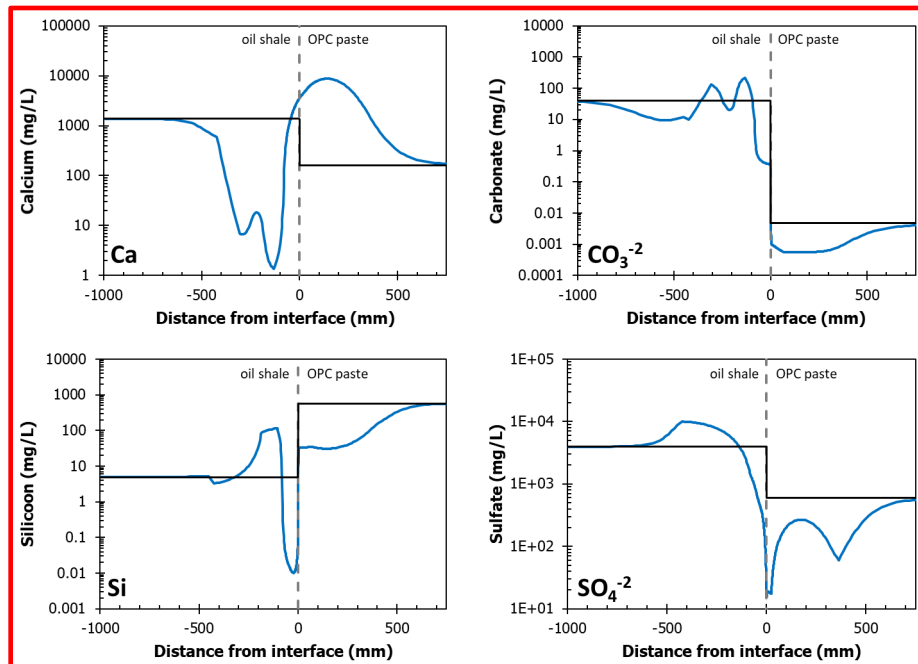




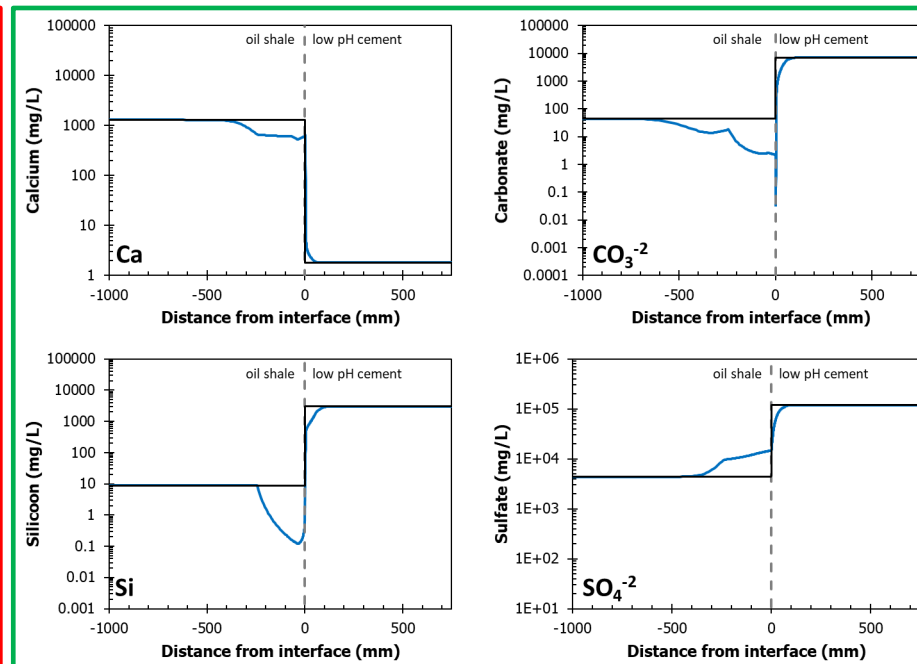
Interface Models Results

Majors Profiles

Oil shale – OPC paste

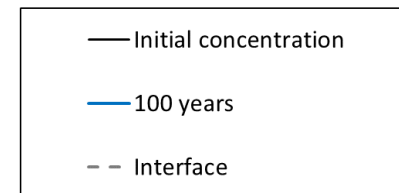


Oil shale – low pH cement



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





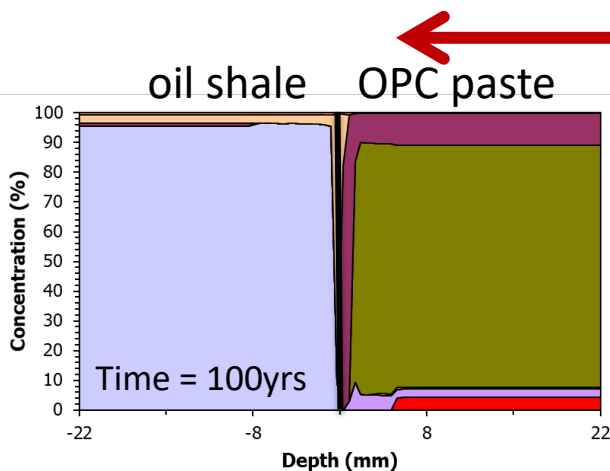
OPC paste Interfaces With Oil Shale/Marl/Limestone

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

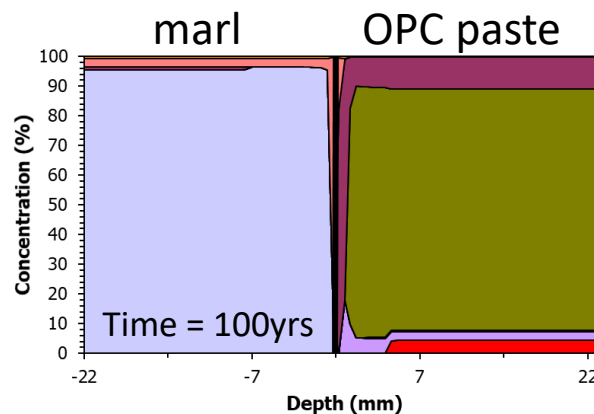
CO_3^{-2} (mol/L)	$3 \cdot 10^{-4}$
ϕ/τ^2	$9 \cdot 10^{-4}$

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

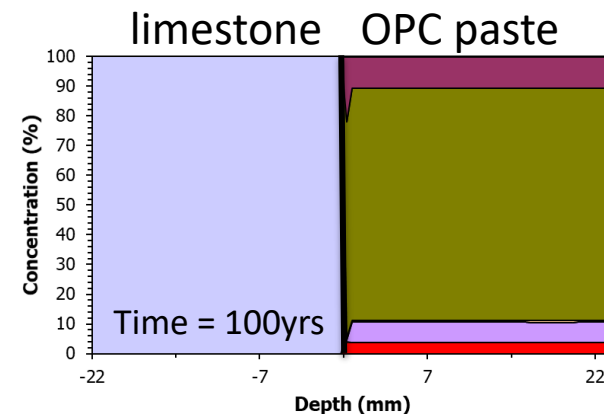
← increasing reactivity



CEM18_CNASH_ss	CEM18_C12A7	CEM18_C3AS0_41H5_18
CEM18_C3FS0_84H4_32	CEM18_Cal	CEM18_Gp
CEM18_Ord_Dol	CEM18_Portlandite	CEM18_ettringite
CEM18_thaumasite	Hydroxylapatite	



CEM18_CNASH_ss	CEM18_C12A7	CEM18_C3AS0_41H5_18
CEM18_C3FS0_84H4_32	CEM18_Cal	CEM18_Gp
CEM18_Ord_Dol	CEM18_Portlandite	CEM18_ettringite
CEM18_thaumasite	Hydroxylapatite	



CEM18_CNASH_ss	CEM18_C3AS0_41H5_18	CEM18_C3FS0_84H4_32
CEM18_Cal	CEM18_Portlandite	CEM18_ettringite
Hydroxylapatite		

Key observations:

- Portlandite and CSH depletion in OPC paste
- Ettringite and Hydrogarnet formation in OPC paste
- Thaumassite formation in rocks (oil shale 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

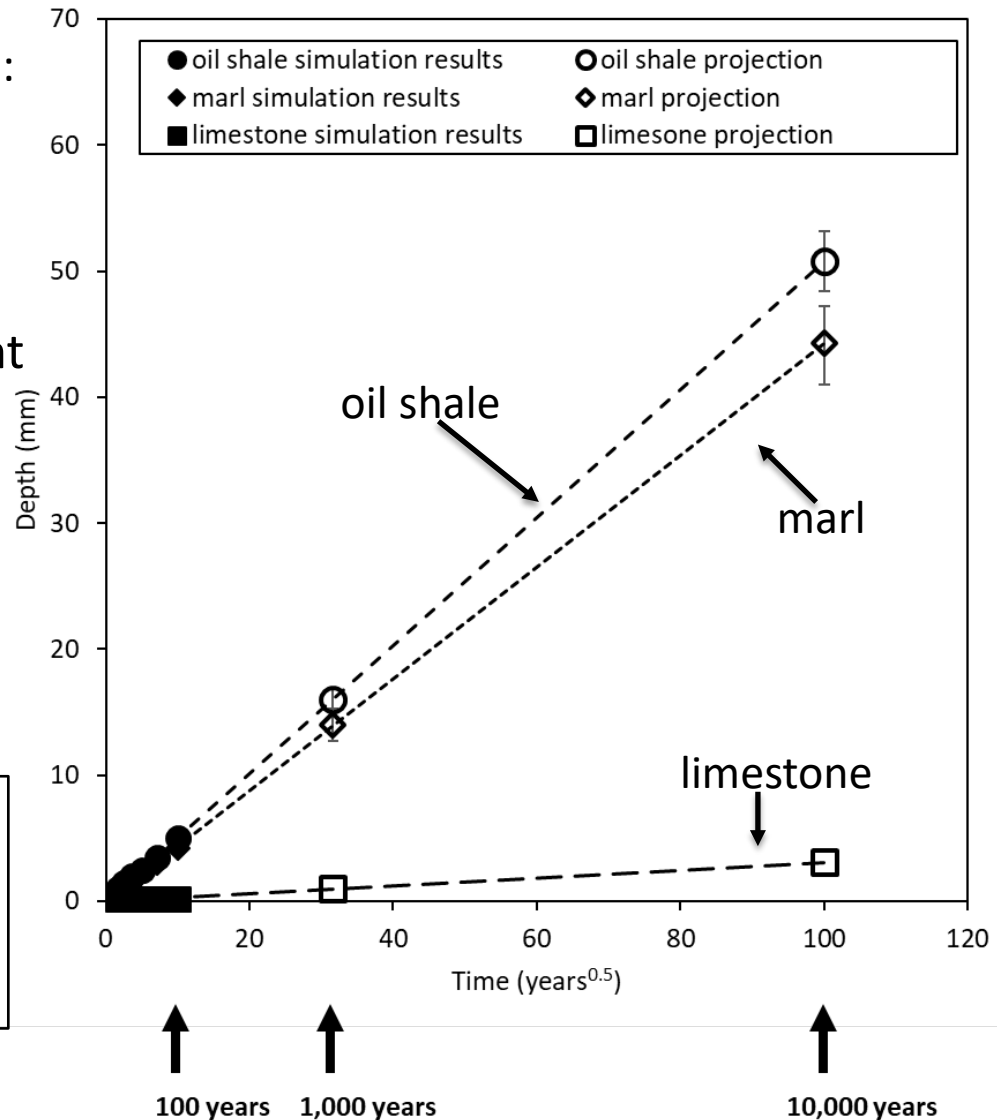


OPC paste Interfaces With Oil Shale/Marl/Limestone

Long-term scenarios (saturated conditions):

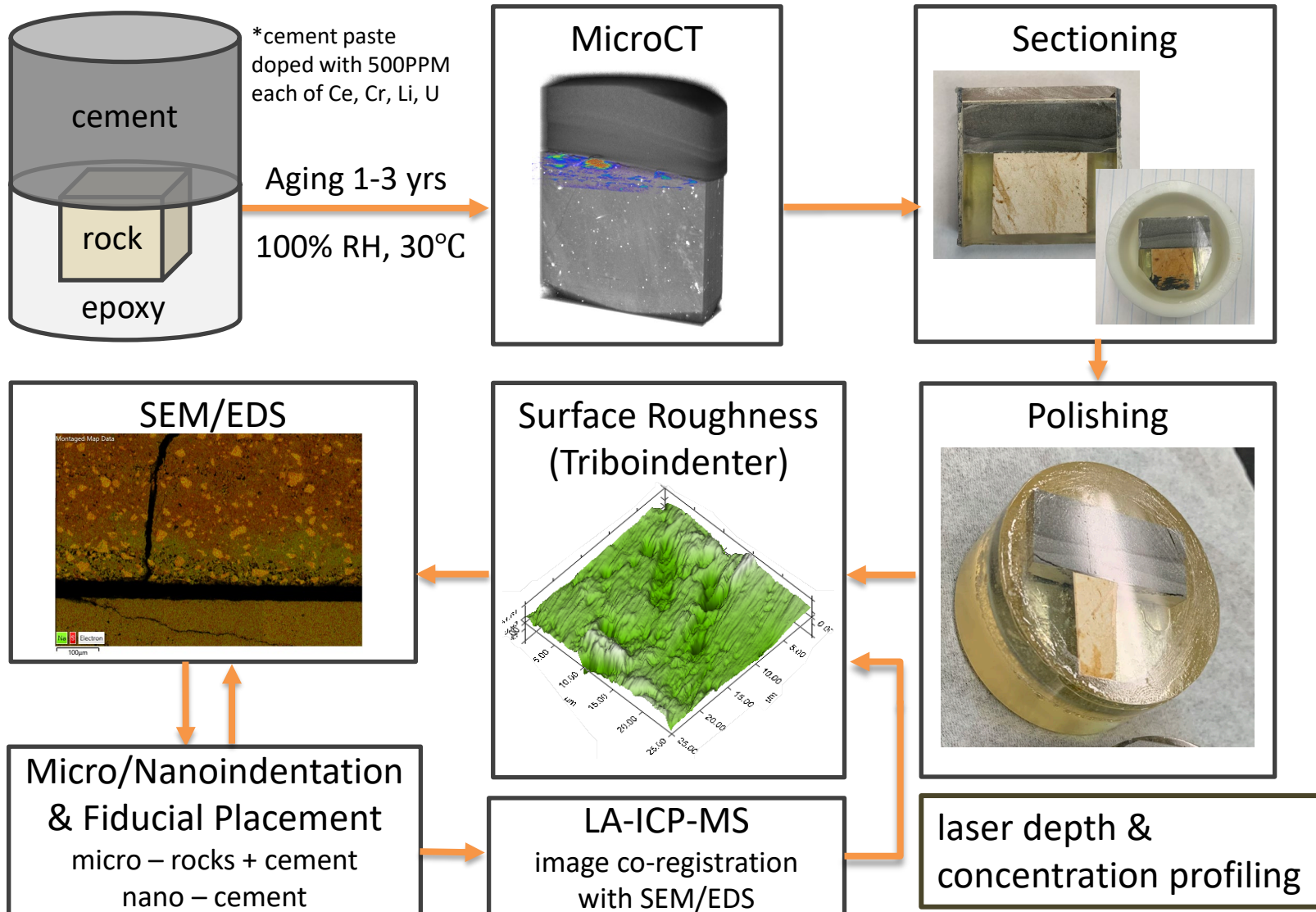
- **Oil shale-OPC:** ~16 and ~51 mm of OPC are carbonated in 1,000 and 10,000 years
- **Marl-OPC:** ~14 and ~43 mm of cement are carbonated in 1,000 and 10,000 years
- **Limestone-OPC:** ~1 and ~4 mm of cement are carbonated in 1,000 and 10,000 years

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)**





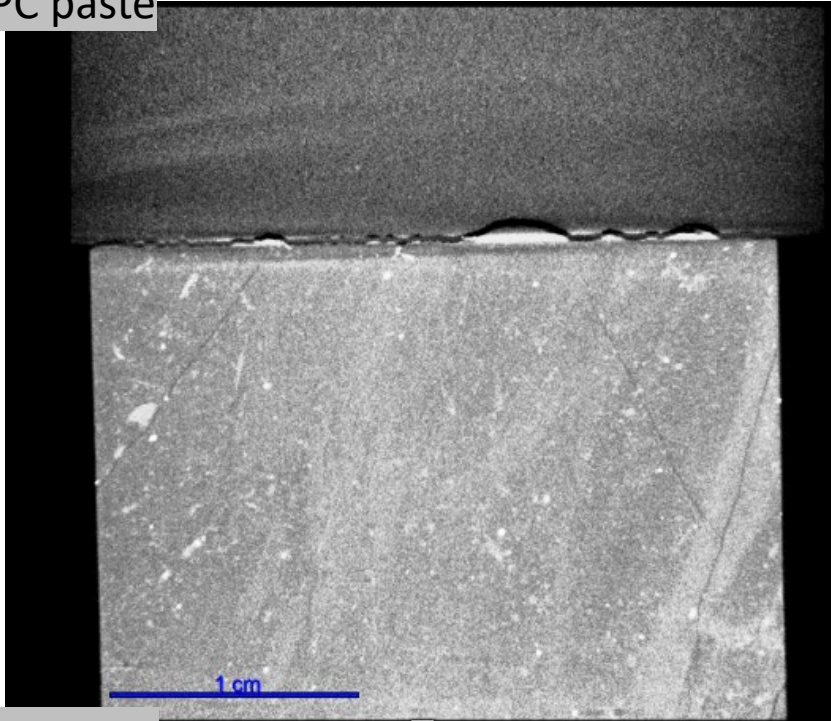
Experimental Project Approach





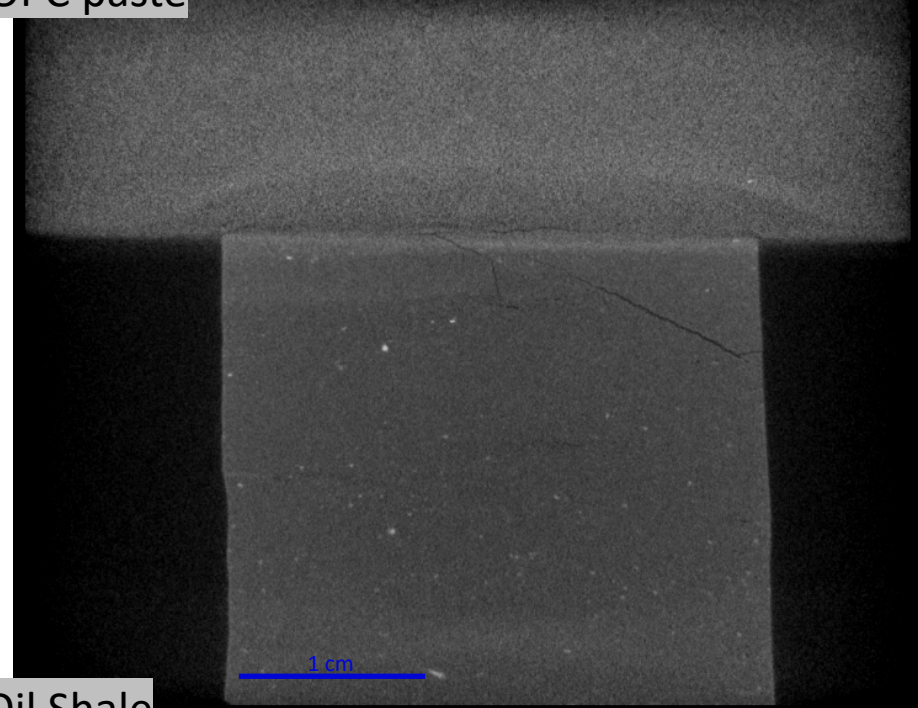
MicroCT

OPC paste



Limestone

OPC paste



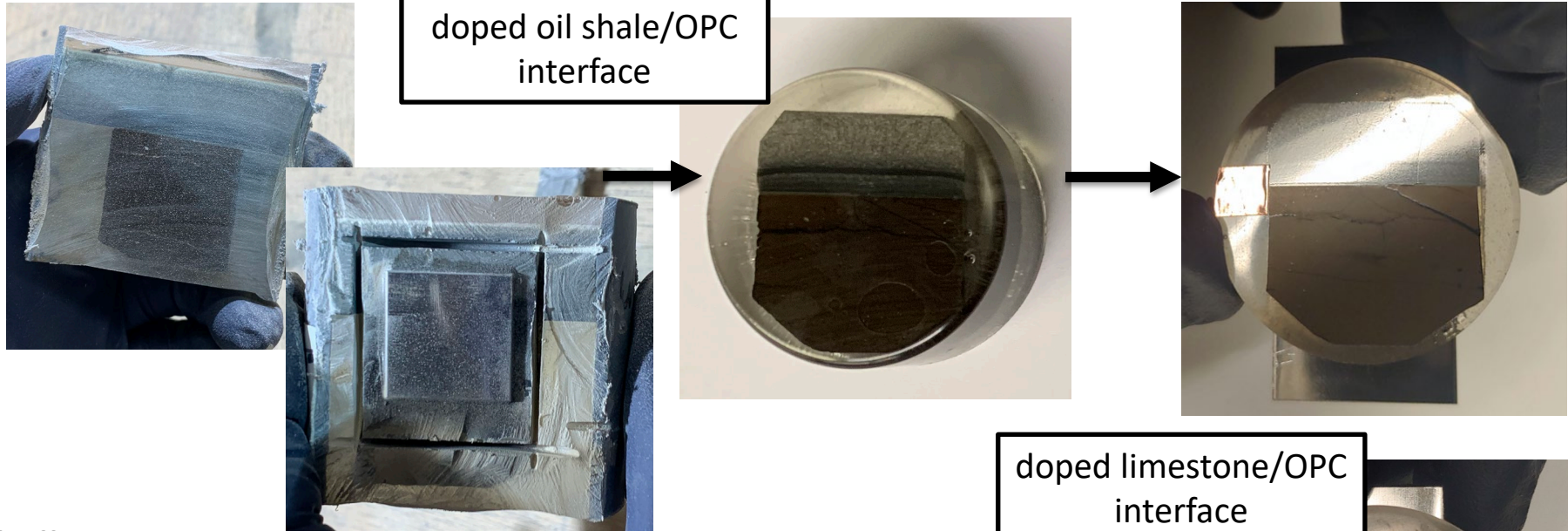
Oil Shale

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



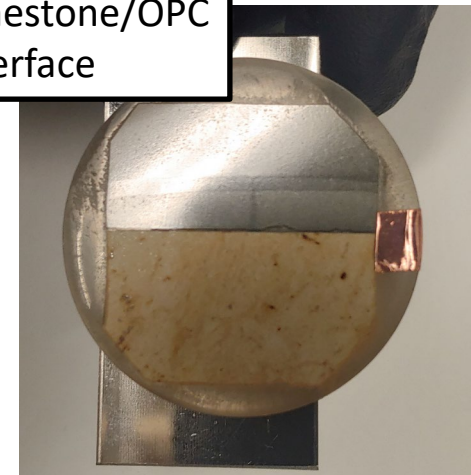
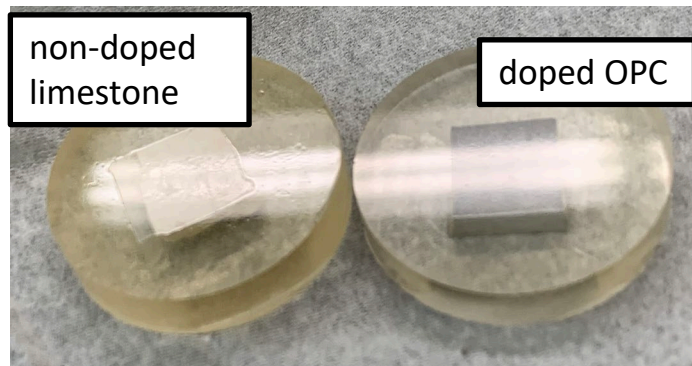
Sample Preparation

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



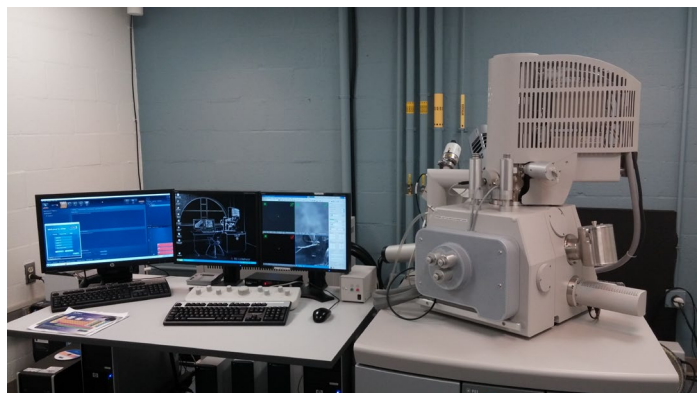
Challenges:

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





SEM/EDS



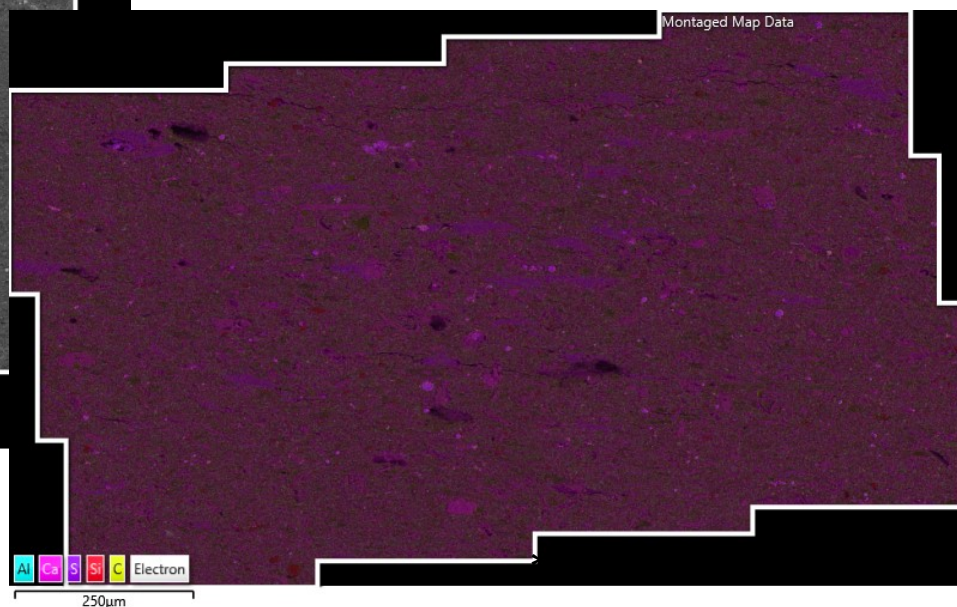
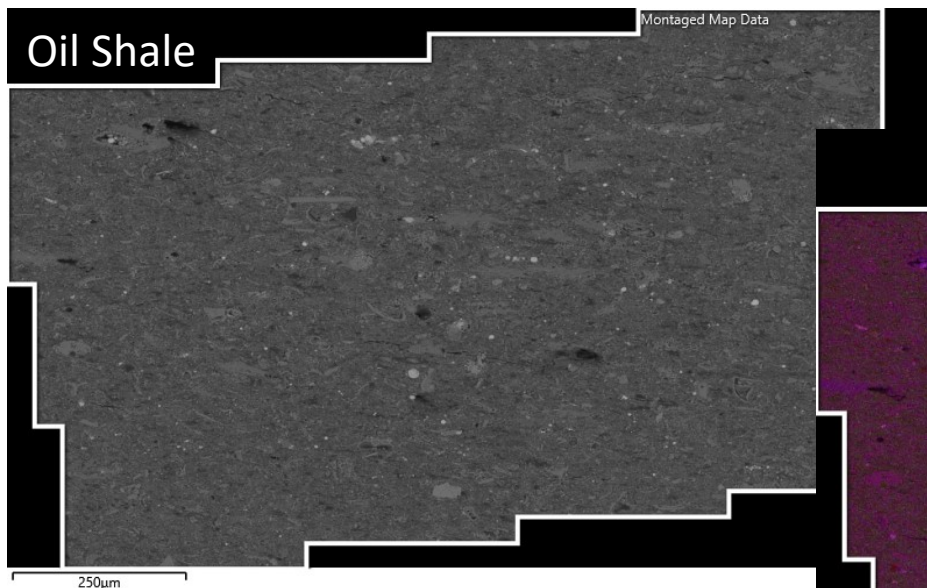
- Large area mapping utilized to investigate microstructure, morphology, and chemistry (major elemental concentrations)

ESEM imaging conditions:

15kV, spot size 3.5, 130 Pa, 600x, pixel dwell time 30 μ s, resolution 1024x874

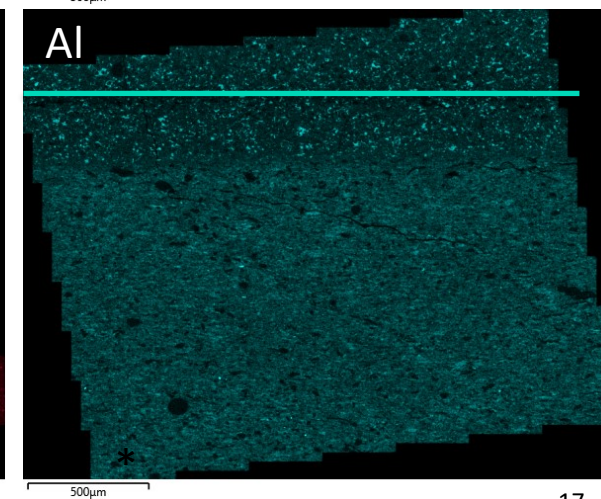
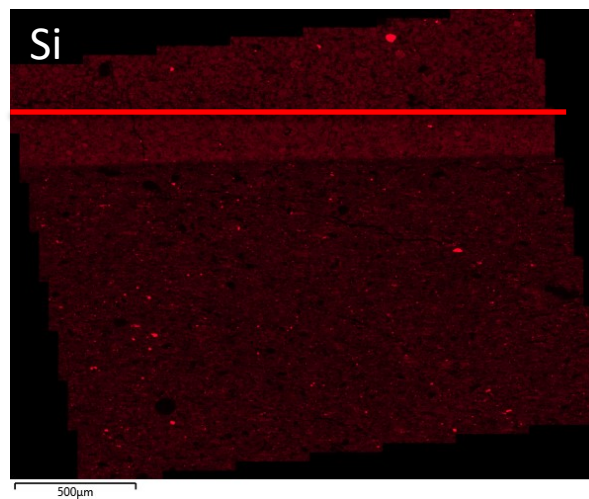
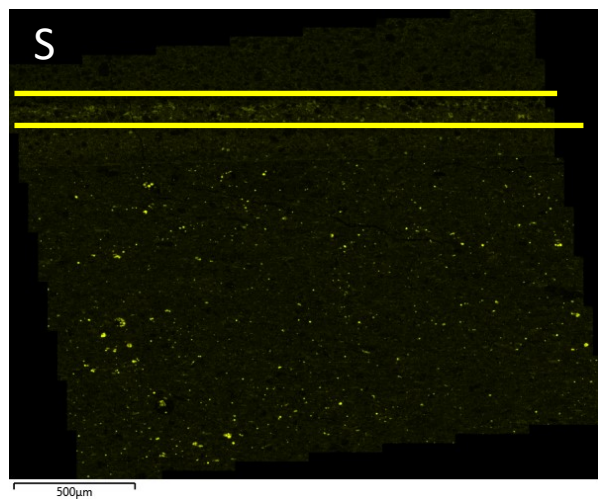
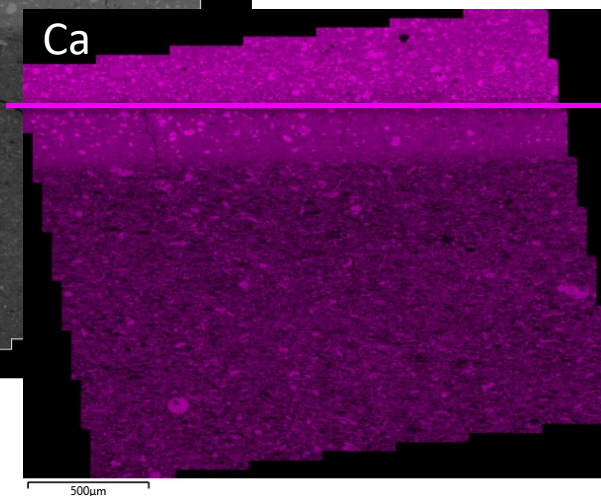
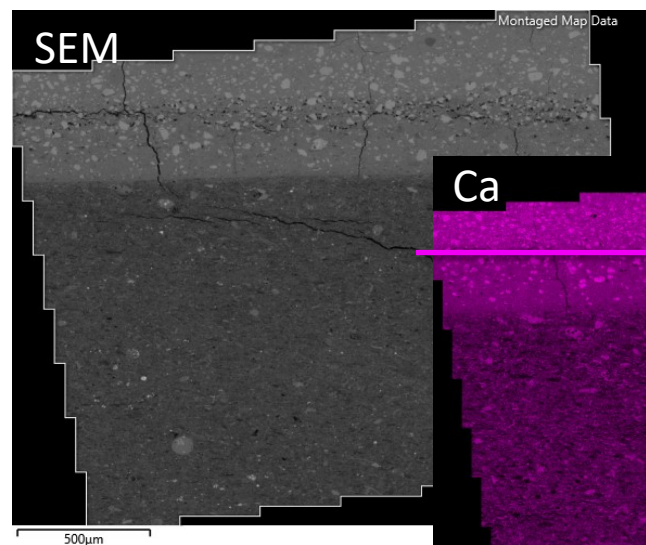
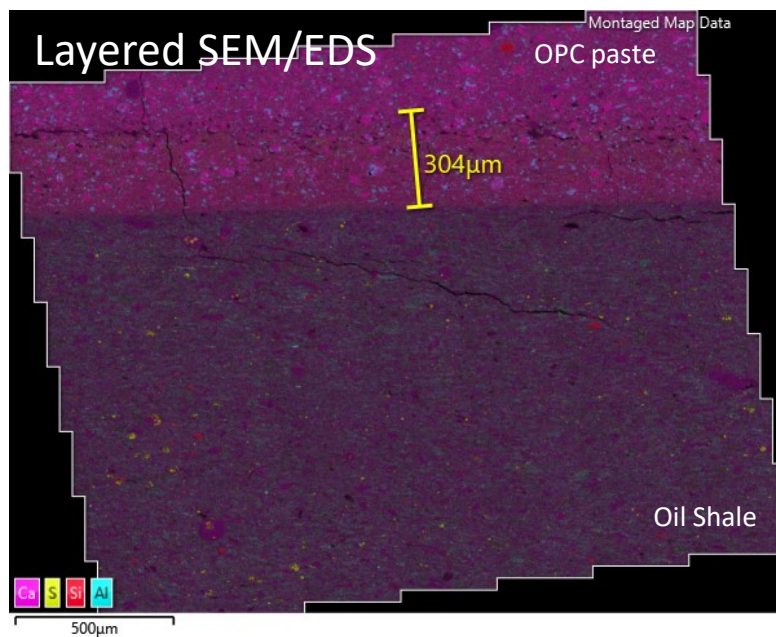
EDS collection conditions:

pixel dwell time 30 μ s, frame count 20, process time 5, resolution 1024x874





SEM/EDS





Nano and Micromechanical Testing



Scanning Probe Microscopy (SPM)

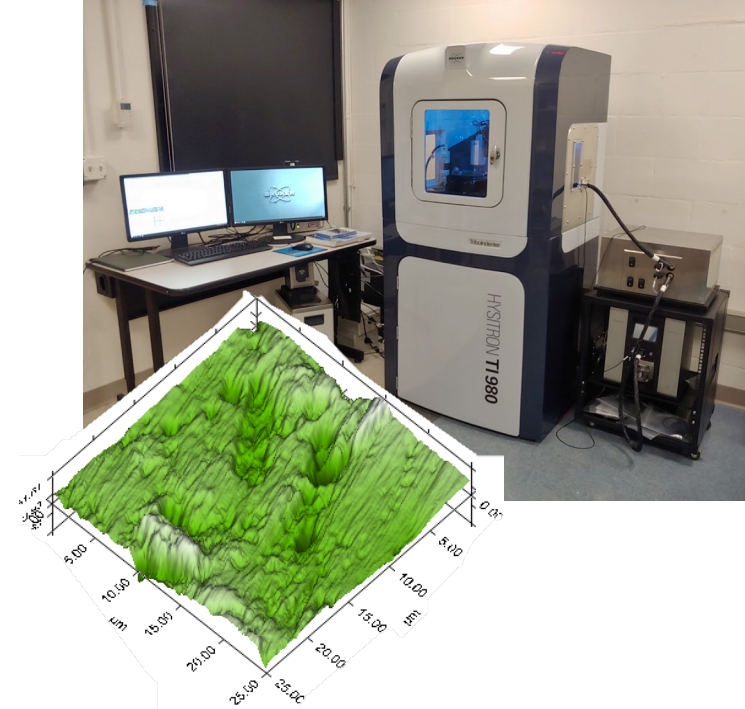
- Provides verification of surface roughness prior to indentation
- Used to map sample surface features

Microindentation

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

Nanoindentation

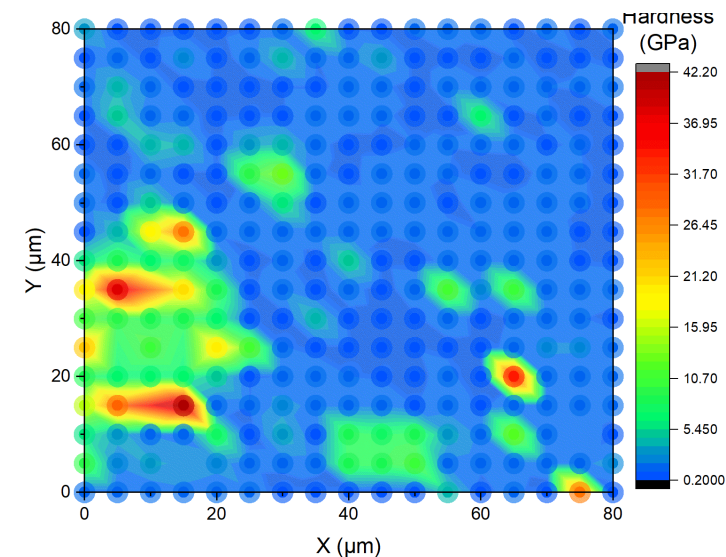
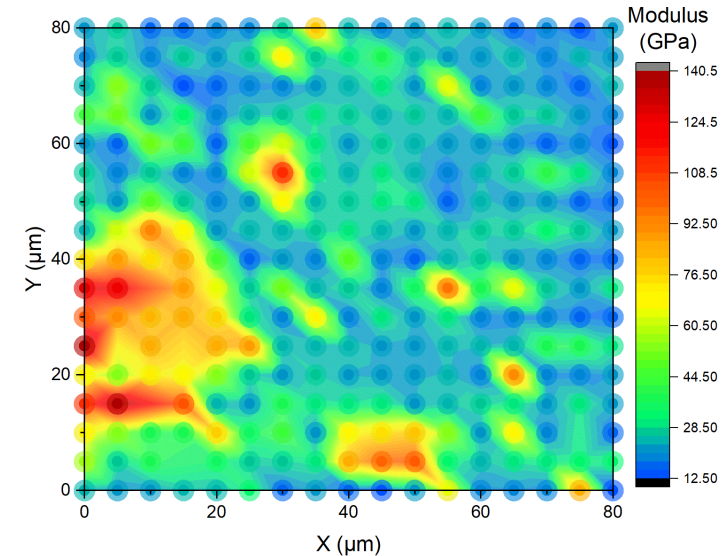
- Accelerated Property Mapping (XPM) to investigate hardness and modulus in close proximity to interfaces
- Grid Nanoindentation to analyze cement phase distribution [upcoming]
 - limited to cement due to dopant influence on rock's ability to polish
 - phase deconvolution will help understand impact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





Accelerated Property Mapping (XPM)

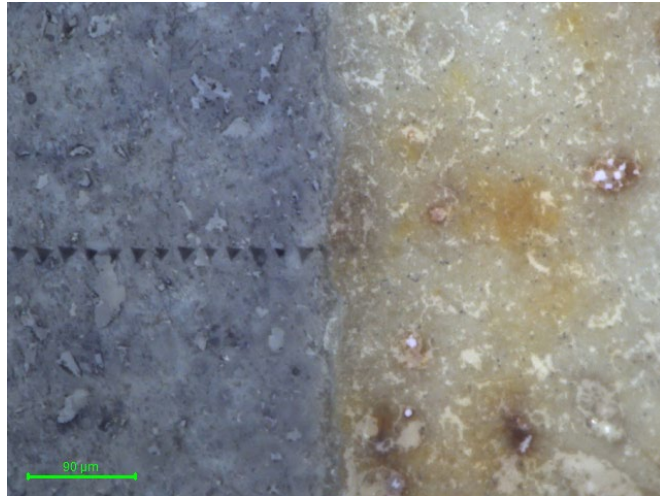
- Piezo controlled movement allows for high-speed collection of nano-mechanical properties as compared to standard grid nanoindentation
 - maximum single-area dimensions $85\mu\text{m} \times 85\mu\text{m}$
- Produces quantitative heat map of measured mechanical properties
- May not account for samples that require extended creep time, or for a sample's strain rate sensitivity





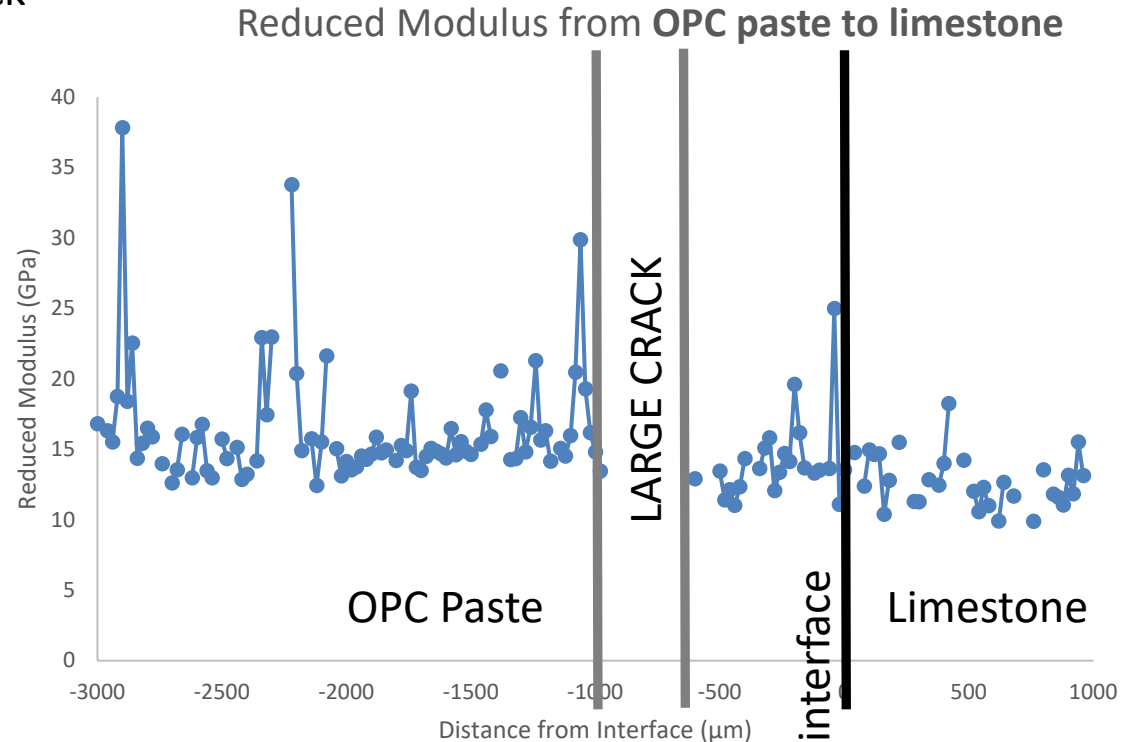
Microindentation

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



Triboindenter Conditions

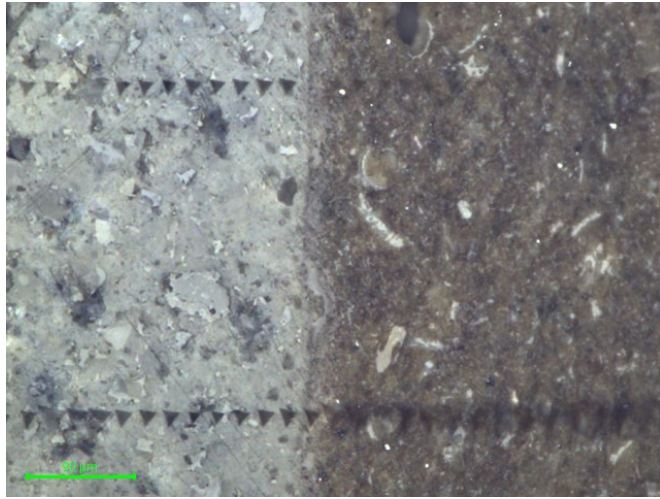
Berkovich tip
peak load 75 mN
10-15-10 sec – trapezoidal load function



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



Microindentation

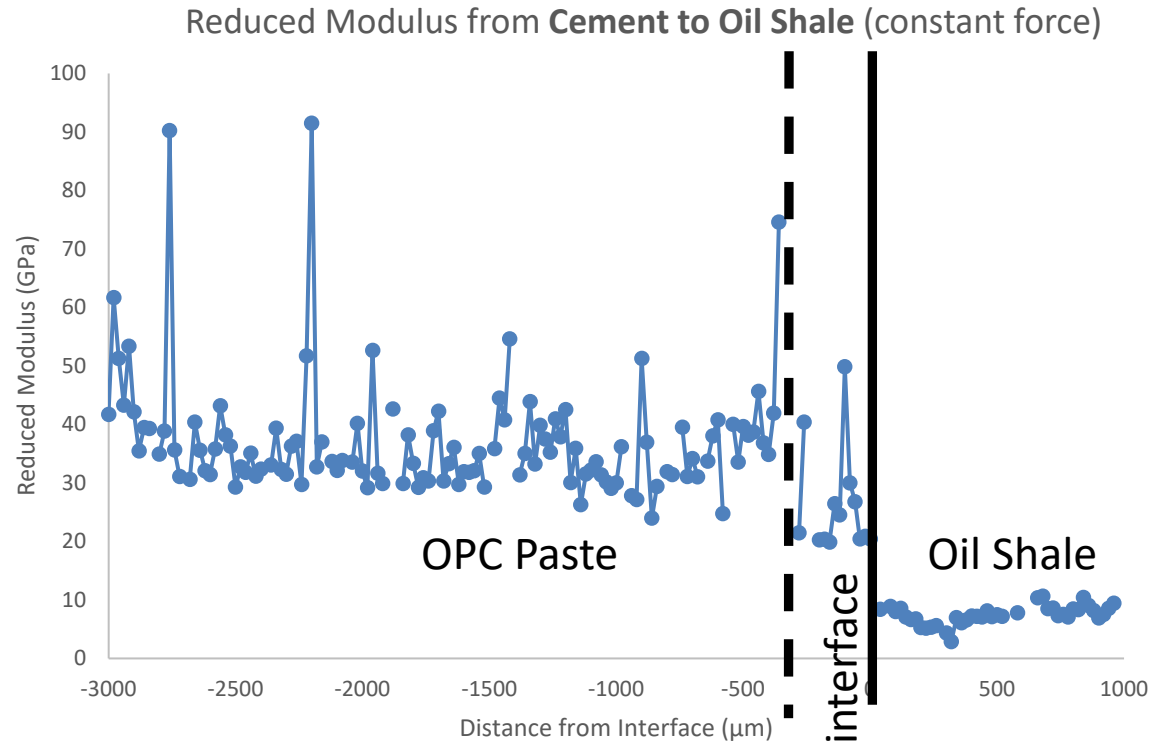


Triboindenter Conditions

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)

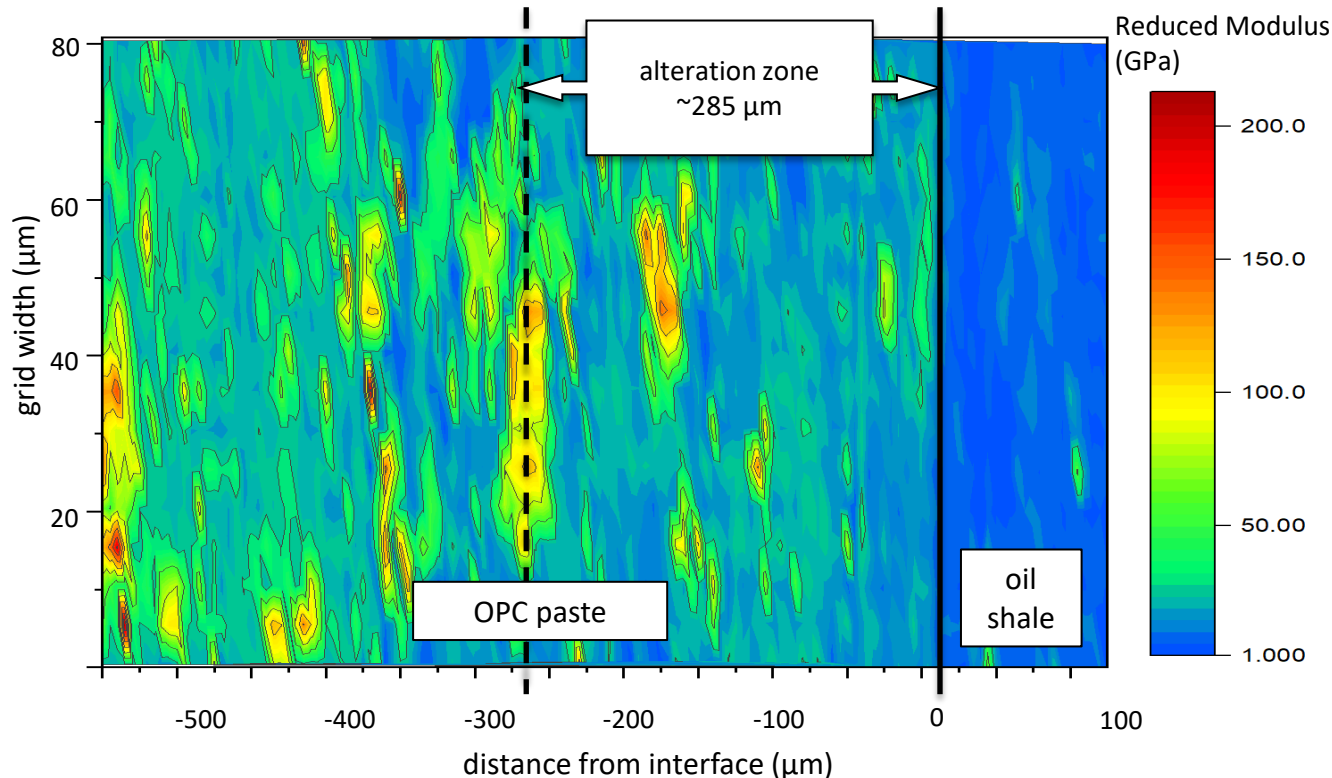
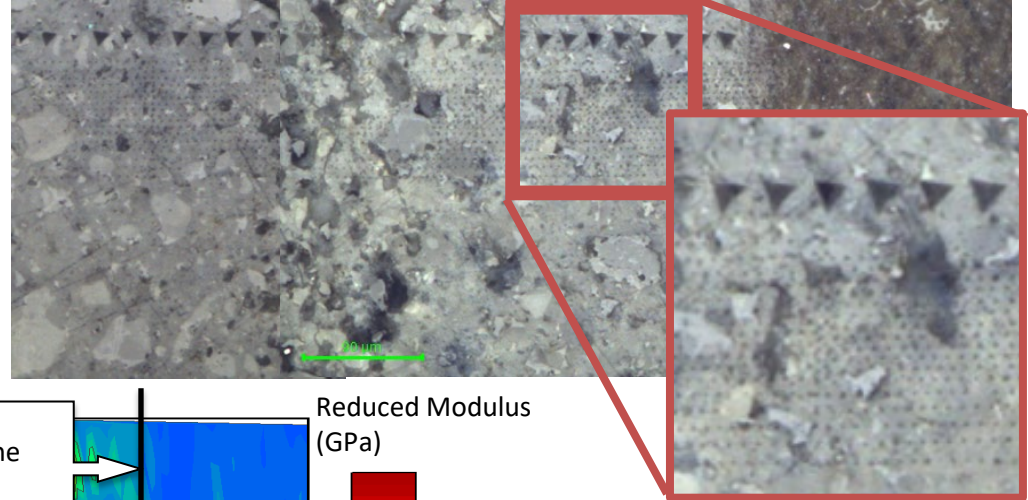
- Series of square grids (85 x 85 μm) crossing over interface region

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 300 μm is estimated
- **Laboratory experiments, chemical data:** elemental gradients in Ca, Si, Al, and S in the OPC paste form an alteration zone of $\sim 300 \mu\text{m}$
- **Laboratory experiments, mechanical data:** suggests reduced moduli values in OPC paste at a depth of $300 \mu\text{m} \pm 20 \mu\text{m}$ 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	300 μm



Future Directions



Experimental:

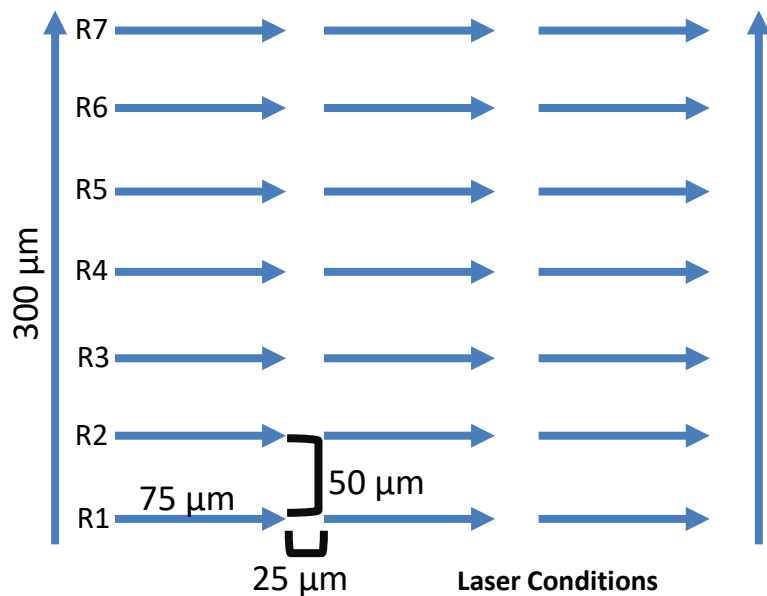
- Currently in advanced stages of designing approach to laser ablation measurements
 - provides quantification of the dopant concentrations as a function of distance from the interface
- Perform grid nanoindentation and analyze data to get mechanical information on the cementitious phases through the 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

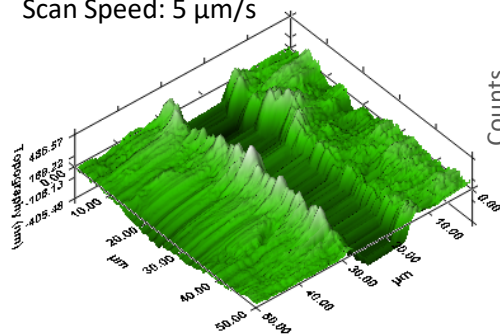
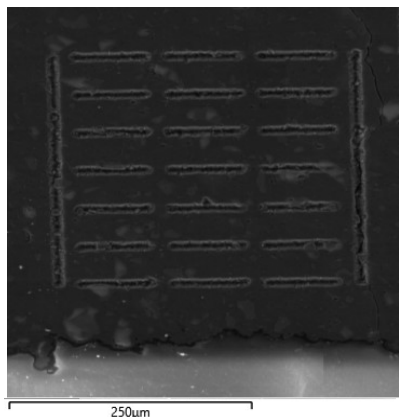


Laser Ablation – Preliminary Results: Limestone-OPC Interface

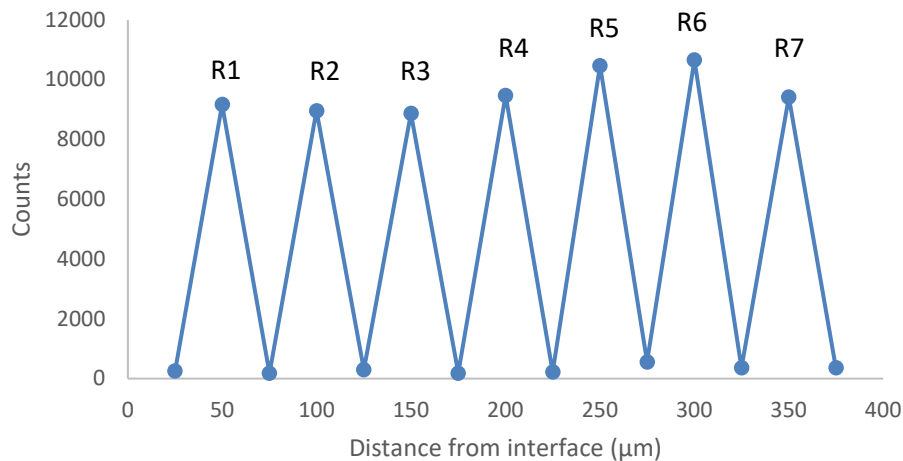


Laser Conditions

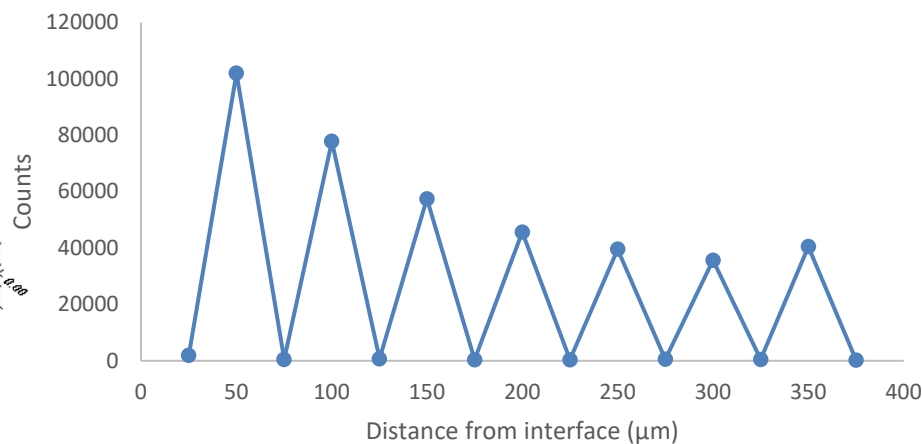
Energy: 7 J/cm²
Frequency: 4 Hz
Spot Size: 10 μm
Scan Speed: 5 μm/s



Ca43 - moving away from interface



U238 - moving away from interface





Acknowledgments



- **McKalee Steen, Rich Teising, Emma Wuerth, and Peng Zheng (Vanderbilt University)**
- **Chven Mitchell for micro-CT images used in this presentation, acquired on a Zeiss Xradia 510 Versa 3D X-ray Microscope that was supported by the EVPRP Major Multi-User Equipment Program 2017 at Purdue University.**