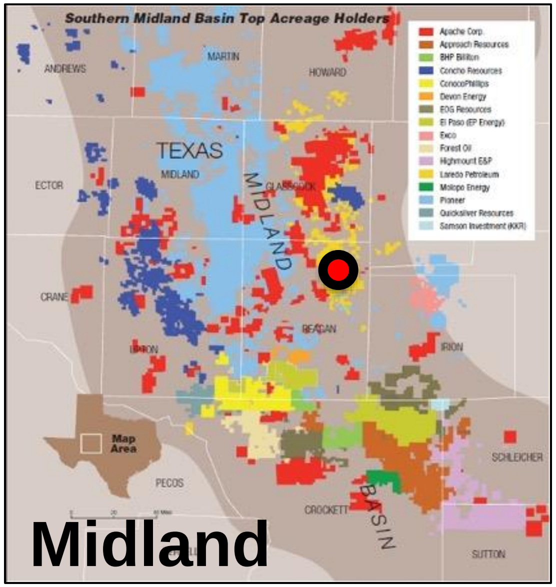
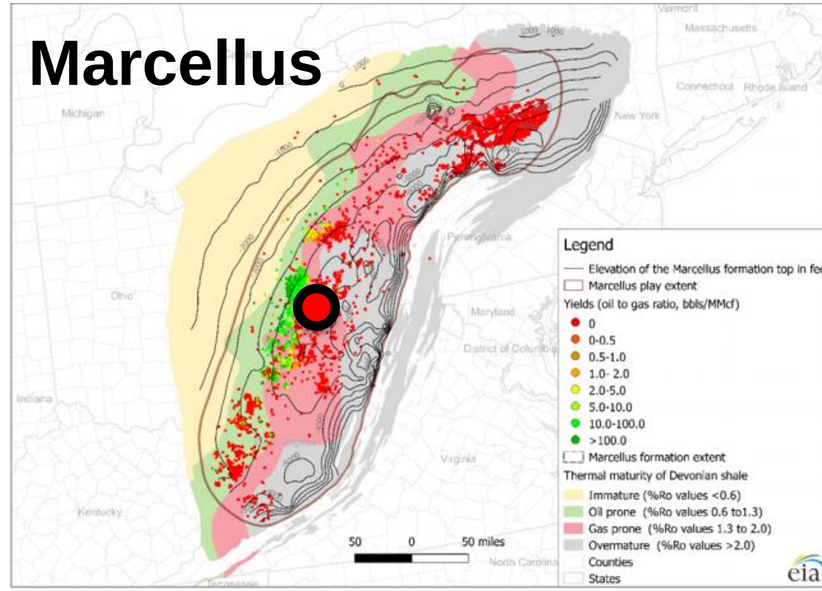
# SLAC NATIONAL ACCELERATOR LABORATORY




# Basin-specific geochemistry to promote unconventional efficiency

**FUNDAMENTAL RESEARCH PROJECT REVIEW MEETING**

U.S. DEPARTMENT OF ENERGY Fossil Energy OFFICE OF OIL & NATURAL GAS

**August 25, 2021**

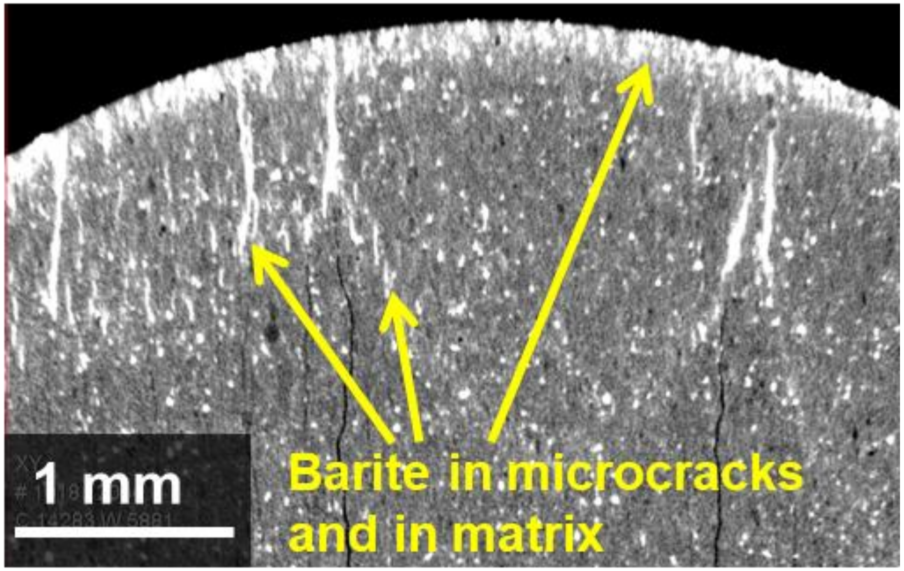
# Barriers to production

1. Precipitation of mineral scale that clogs fracture faces & (micro-)fractures

2. Unfavorable composition of (recycled) water and brine used for stimulation

3.  Unforeseen consequences of additive use/degradation

4. *Very* low intrinsic permeability

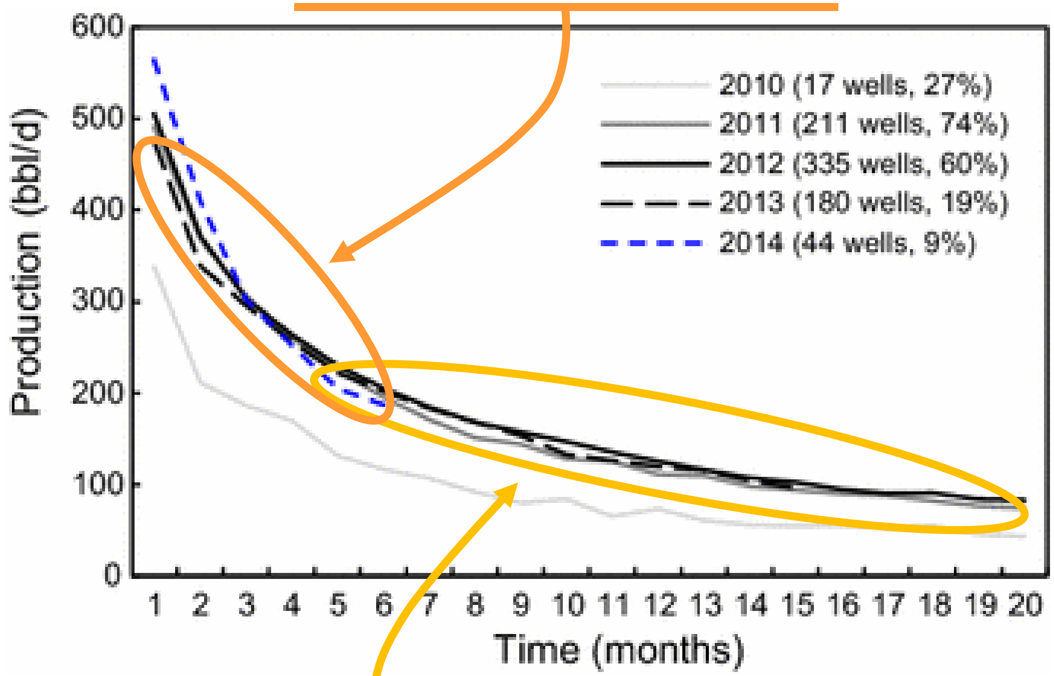


# Important knowledge gaps

**What geochemical parameters control mineral scale - in different basins?**

**Can we monitor mineral scale and fractures simultaneously?**

**How can we mitigate unconventional mineral scale?**




Wachtmeister *et al* (2017) *Nat. Resour.Res*

**Can we manipulate porosity to improve flow through fracture faces?**

# **Goal:** Develop and embed shale-fluid geochemical knowledge in literature and industrial best practices

SLAC

Progress →

## Basins

**Develop basin-specific geochemical fluid-shale reaction models**

- Marcellus Basin
- Wolfcamp & Permian Basin
- Bakken Formation
- Tuscaloosa shale

## Fluid composition

**Basin-specific fluid optimization for scale management**

- CT imaging of dynamic porosity/perm evolution
- Sulfate mineral scale — *in progress*
- Acid concentration — *in progress*
- Iron control
- Cross-linkers — *in progress*

## Model development

**Improve shale-fluid reactive transport model capabilities**

- Reaction networks, rates
- Chemistry + reactive locations
- Sensitivity analysis
- Link porosity to permeability — *in progress*

## Upscaling

**Implement geochemical knowledge at scale**

- Seismic monitoring of porosity evolution
- HFTS test project LBL, LLNL, SLAC, NETL
- Develop seismic rock physics model — *in progress*
- Reservoir-scale seismic monitoring of porosity alteration
- Reservoir management LANL collaboration

# Team

**Esteves**

Geochemical modeling

**Spielman-Sun**

Experimental geochemistry

**Ding**

Rock physics

**Clark**

Rock physics

**Gundogar**

Fluid transport

**Noël**

Experimental geochemistry

**Bargar**

Experimental geochemistry

**Jew**

Experimental geochemistry

**Druhan**

Geochemical modeling

**Kovscek**

Fluid transport

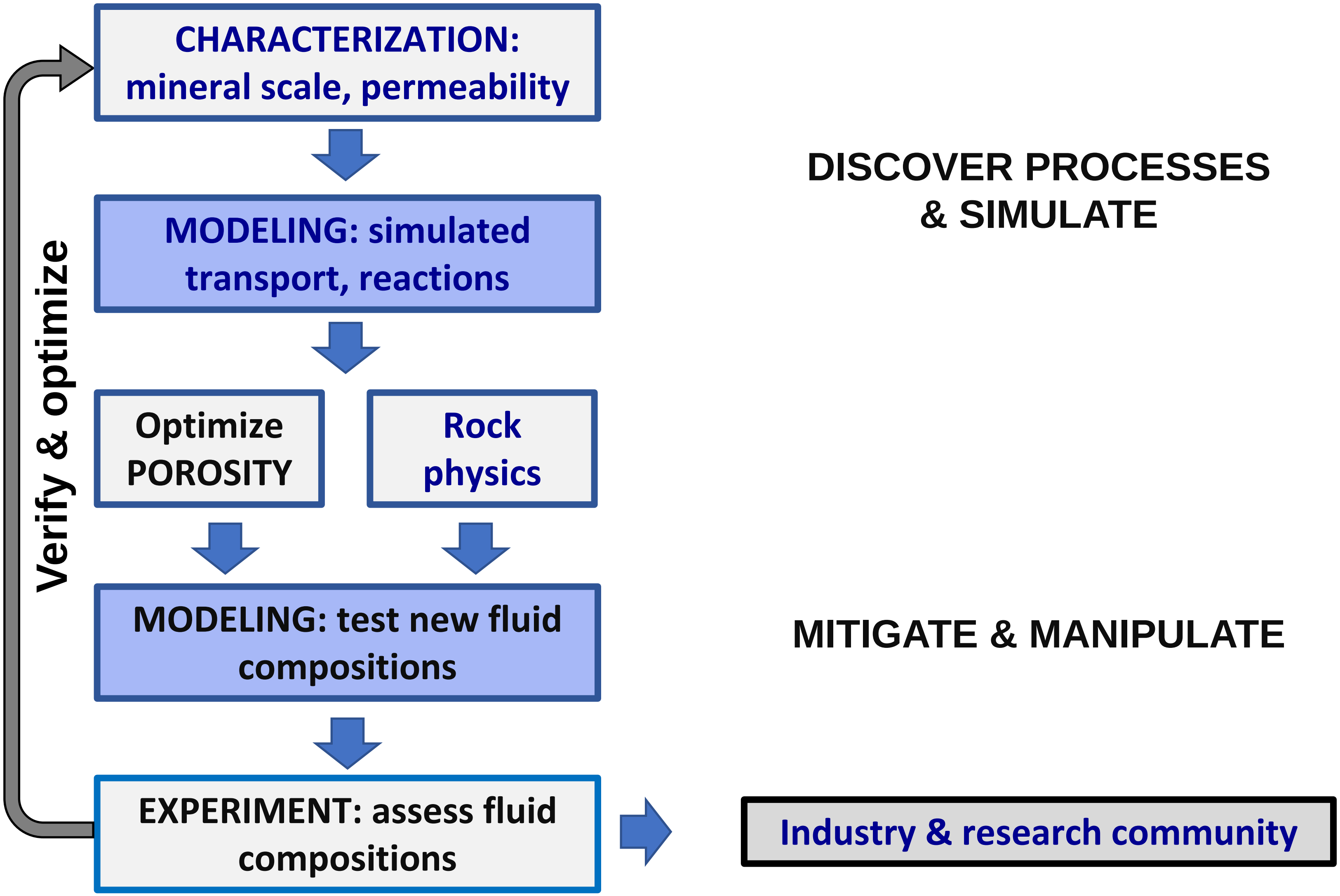
**Vanorio**

Rock physics

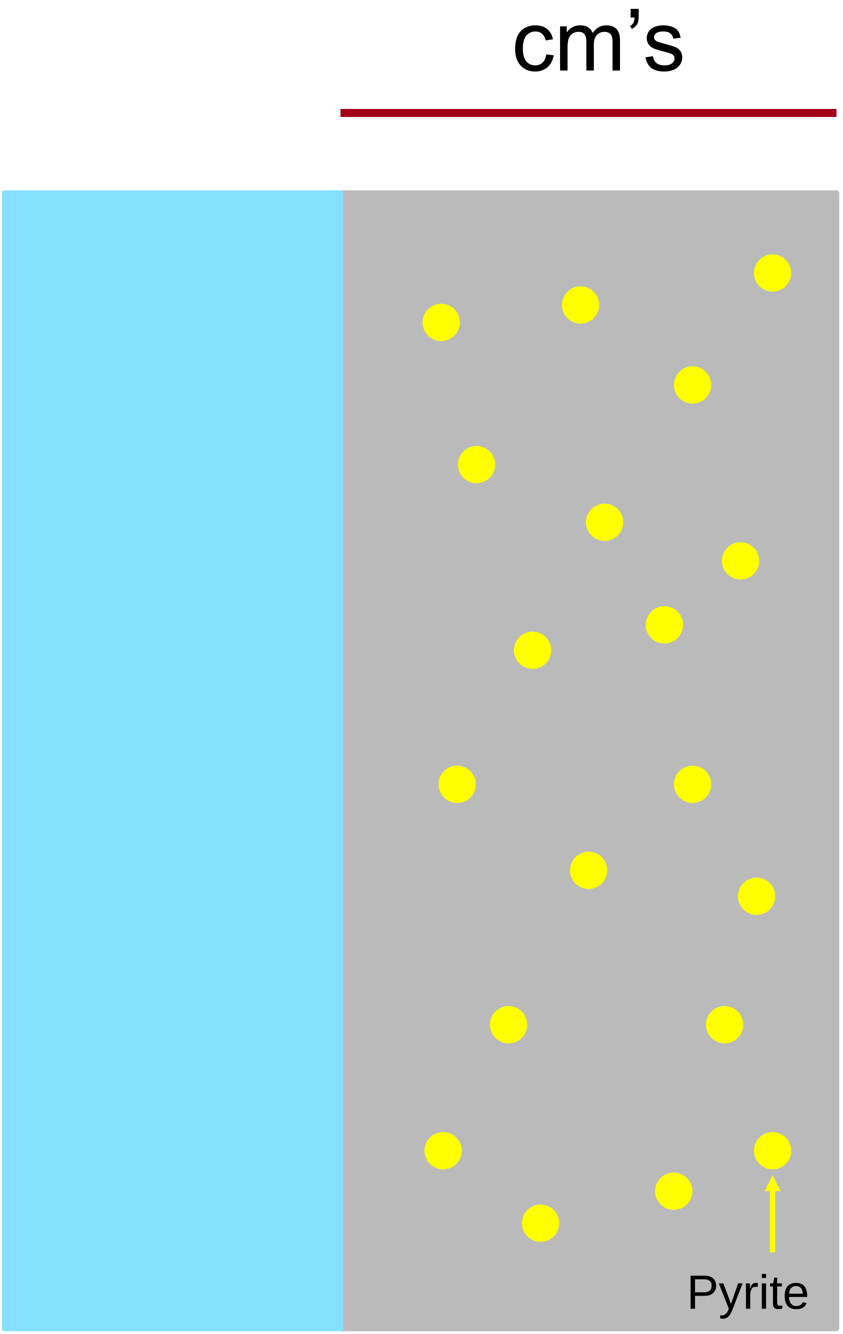
**Brown**

Experimental geochemistry

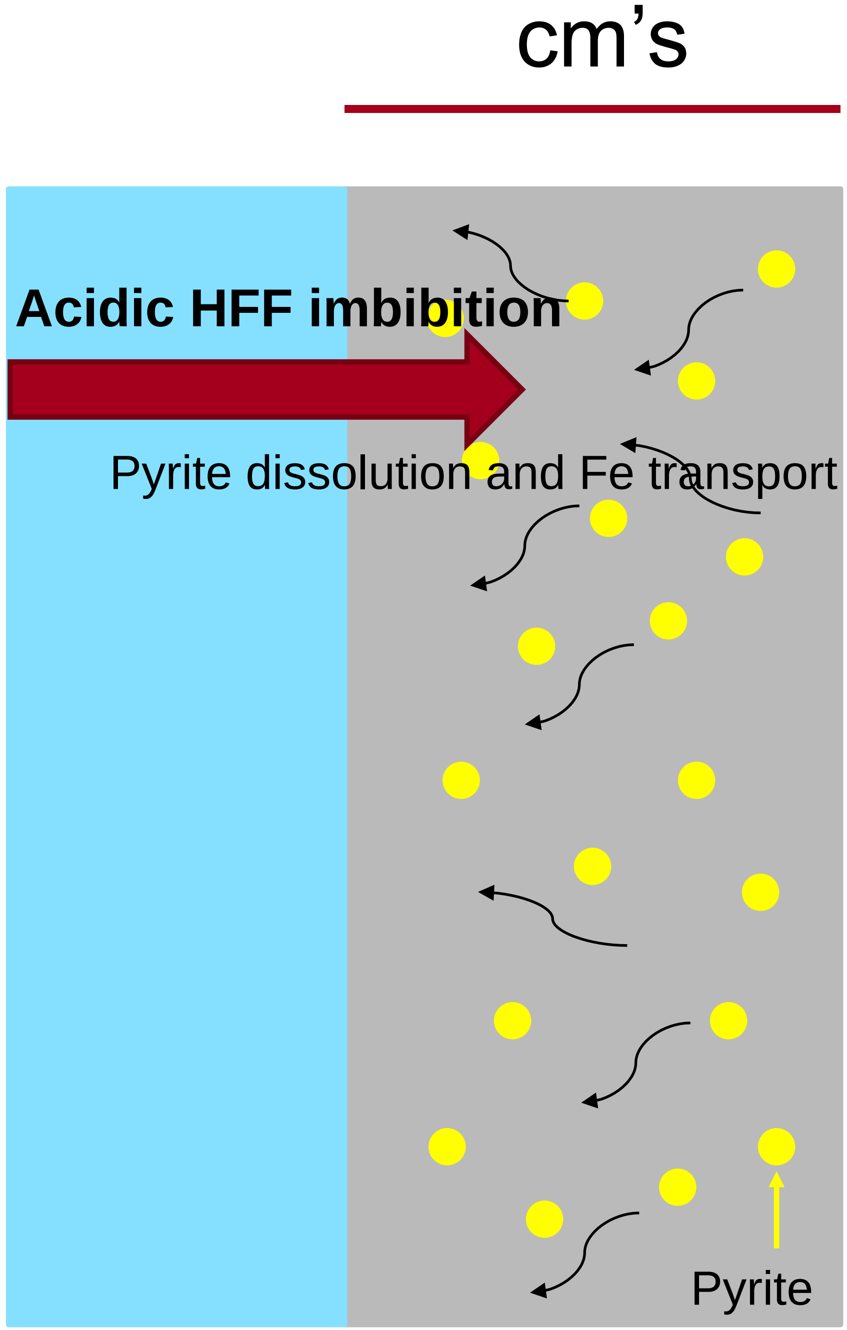
# Understand and Mitigate Mineral Scale



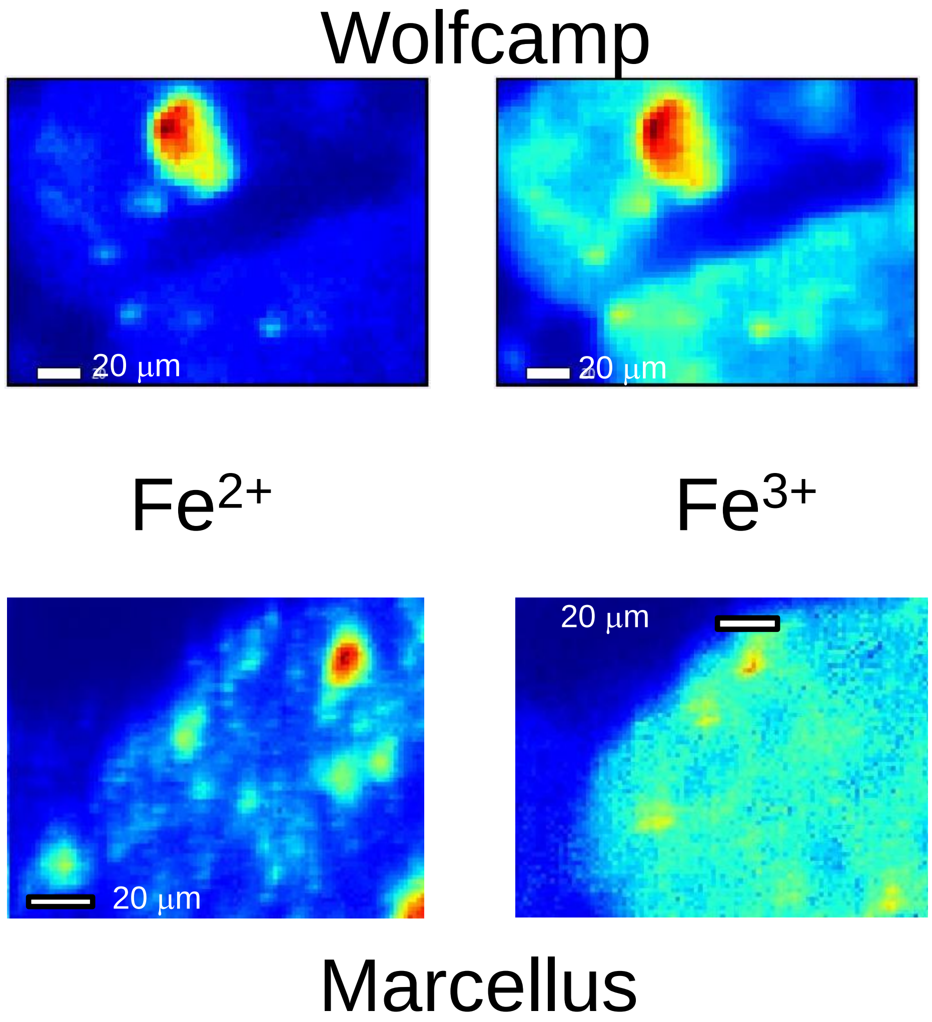
Two ways of Scale Formation: Matrix to surface vs. Solution to Surface

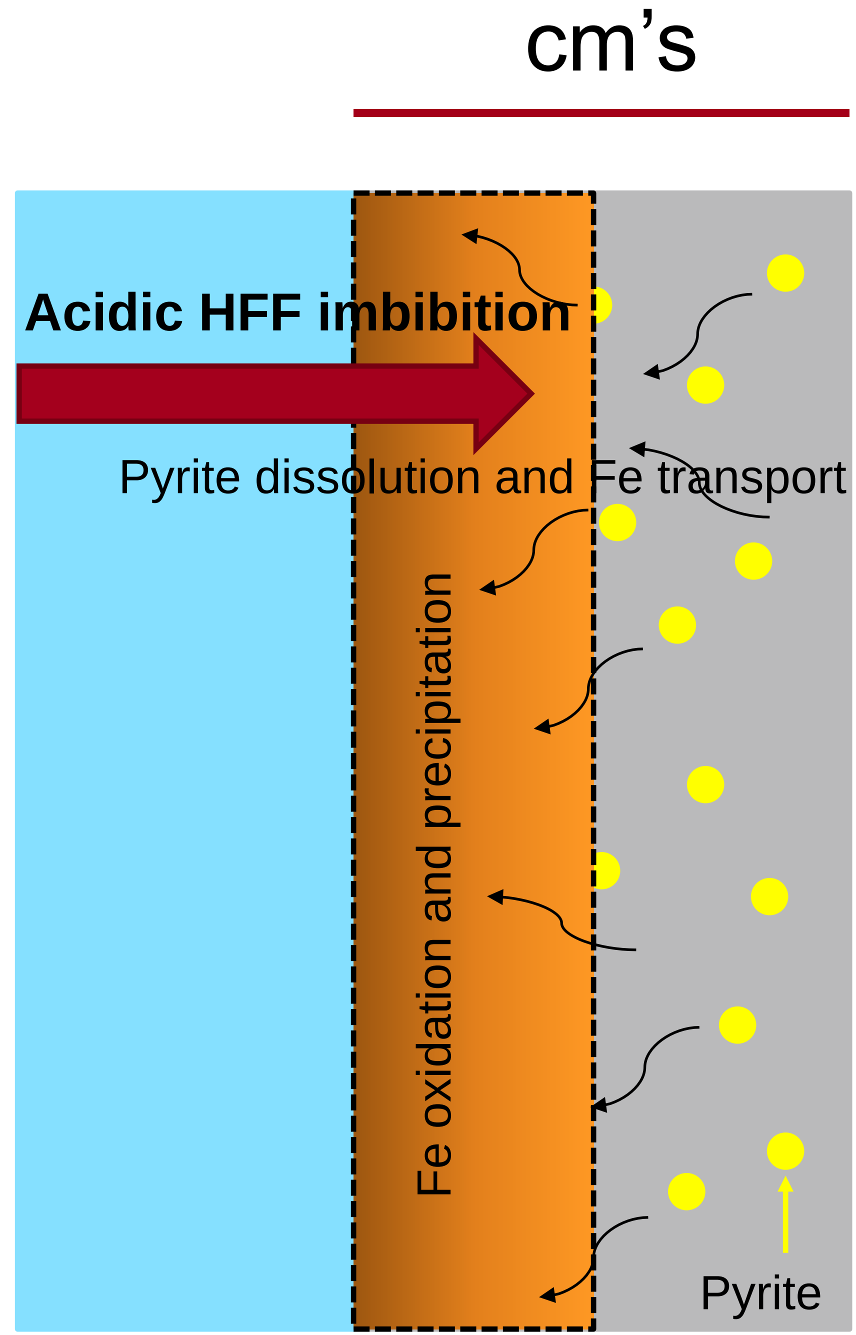


Two ways of Scale Formation: Matrix to surface vs. Solution to Surface

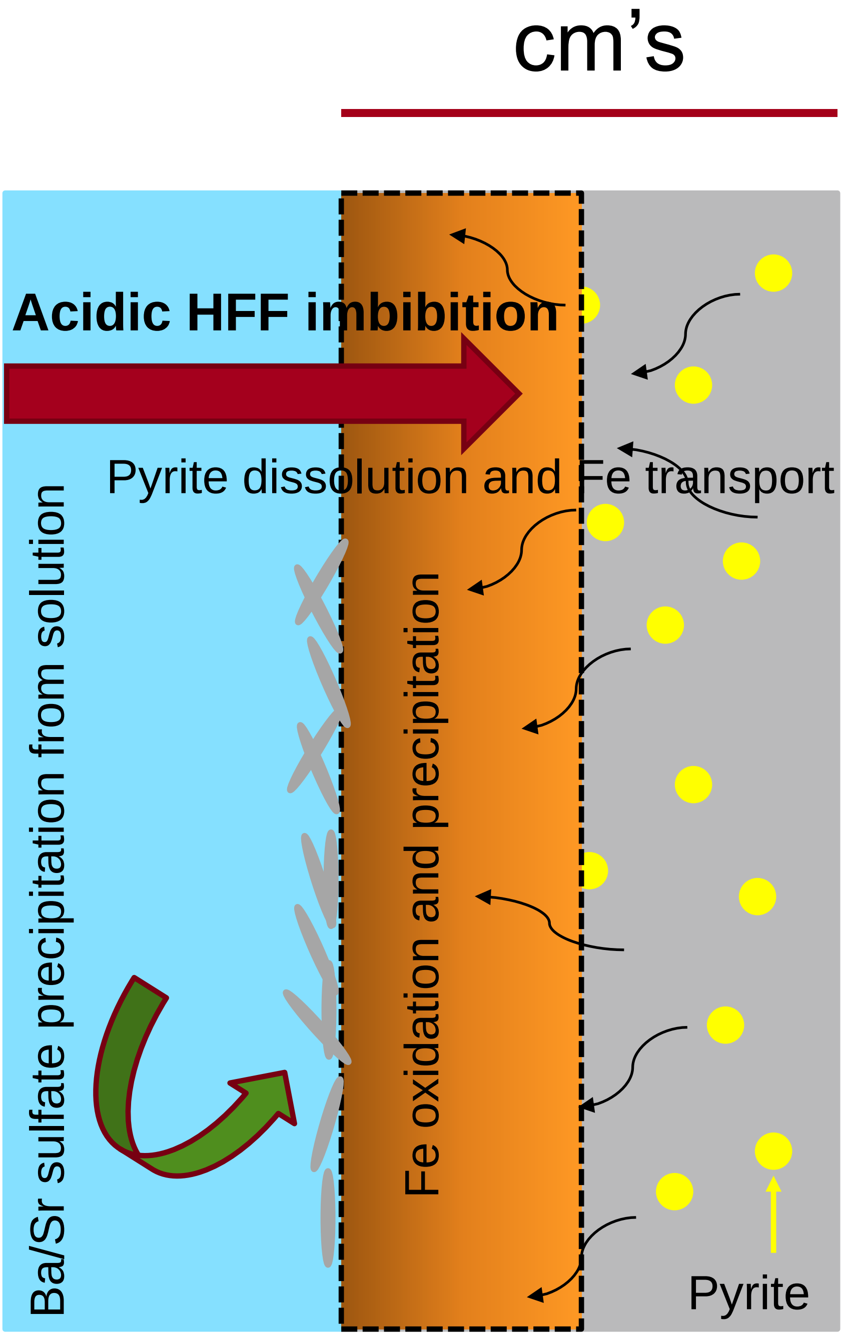


# Two ways of Scale Formation: Matrix to surface vs. Solution to Surface



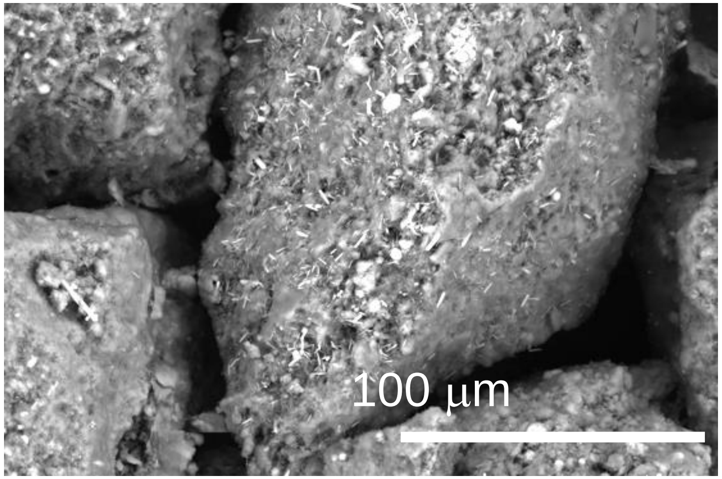



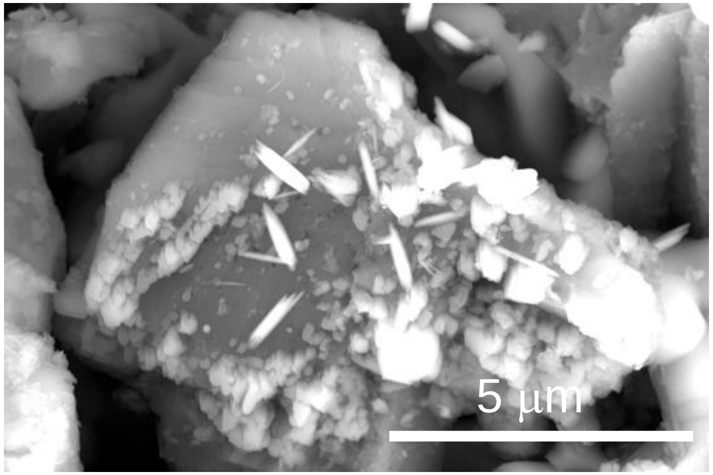
Two ways of Scale Formation: Matrix to surface vs. Solution to Surface

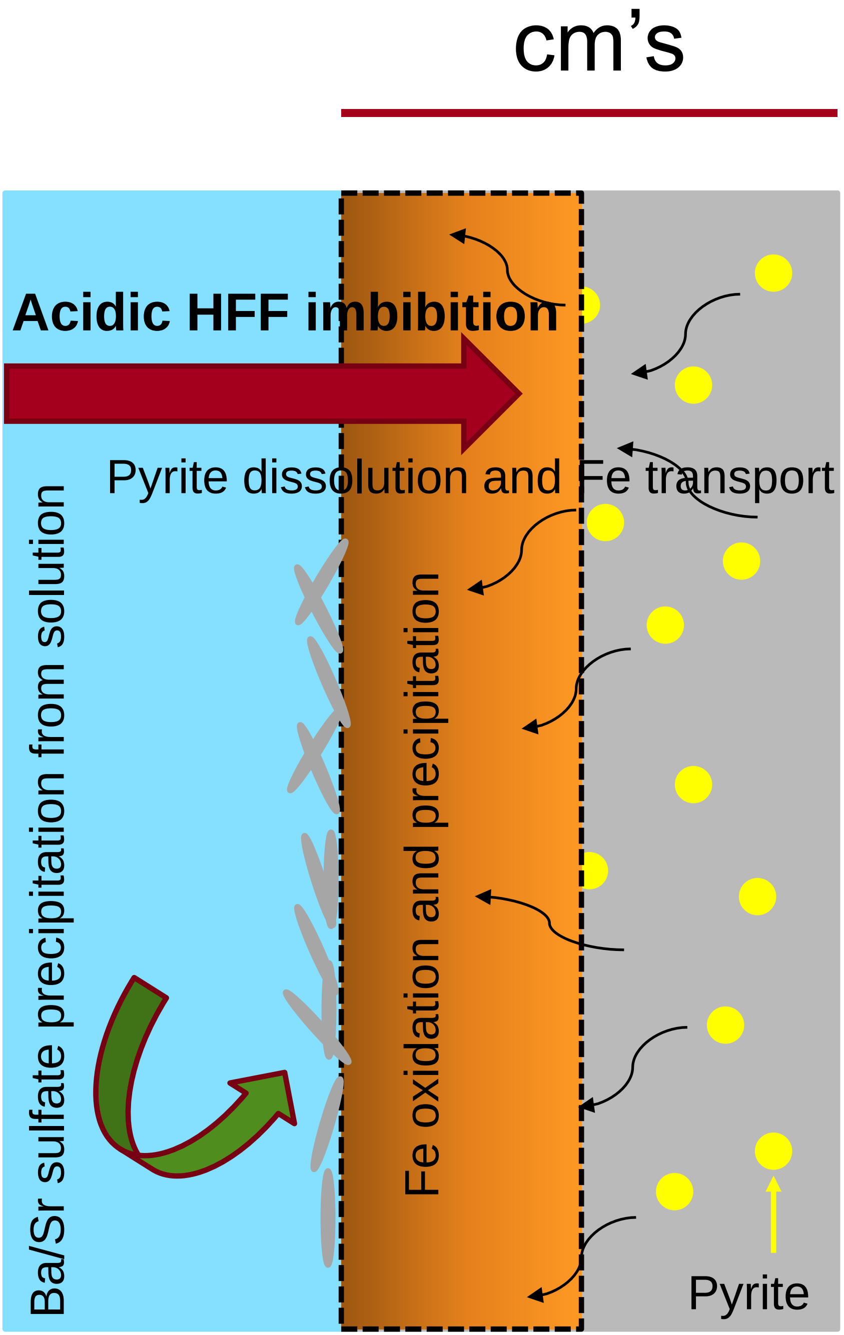


Two ways of Scale Formation: Matrix to surface vs. Solution to Surface

## Wolfcamp



# Characterization & Simulation



**CHARACTERIZATION: mineral scale, permeability**

↓

**MODELING: simulated transport, reactions**

↓

**Optimize POROSITY** | **Rock physics**

↓ ↓

**MODELING: test new fluid compositions**

↓

**EXPERIMENT: assess fluid compositions** → **Industry & research community**

Verify & optimize

**What are the most important forms of mineral scale & What are the controlling reactions?**

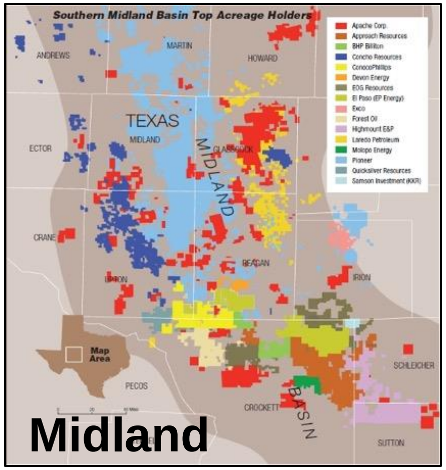
Druhan

Jew

Li

Spielman-Sun

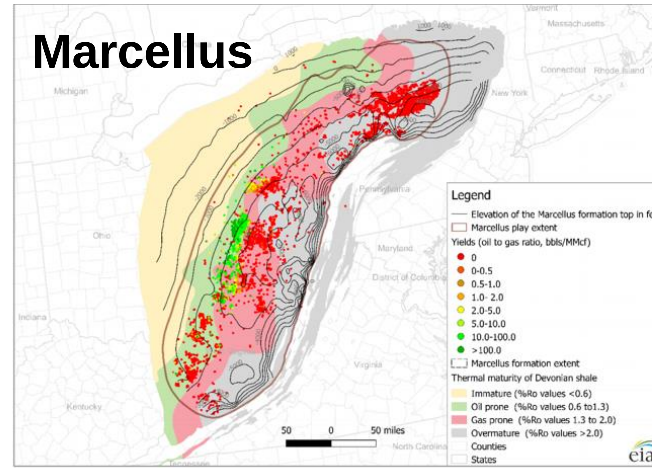
# Sulfate scaling is basin specific




Jew *et al.* (2020)

**$SrSO_4$ scale generally more important**

**$BaSO_4$ scale generally more important**




Jew *et al.* (2019)

**Sr source**

- Clean Brine, Fm. water, shale

**Ba source**

- Drilling mud dissolution
- Drilling mud dissolution, shale

**Sulfate source**

- Breakdown of additives
- Drilling mud dissolution

- Base fluid: $SO_4$-rich river water
- Drilling mud dissolution

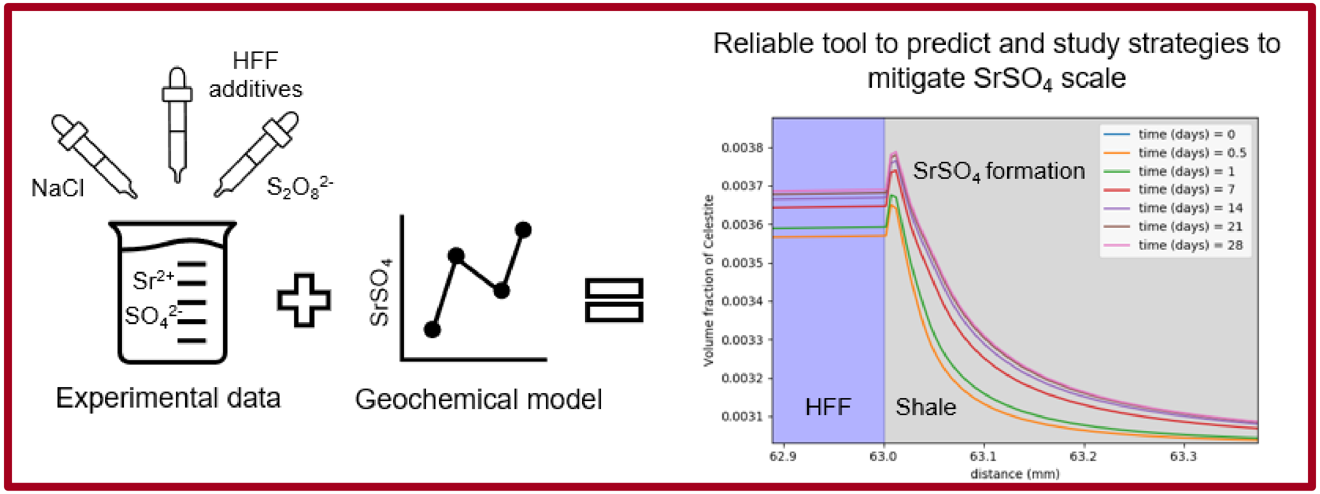
Barite is universal problem; *Degree of problem* is *basin specific*

# Quantitative prediction of celestite precipitation in hydraulic fracturing fluid systems



Celestite (**$SrSO_4$**) precipitation is an unresolved secondary mineral scaling problem in hydraulic fracturing systems, especially in basins where large concentrations of naturally occurring strontium are present (**Midland Basin**).

- A global model capable of predict celestite formation in shale formations is developed and validated.
  - **Experimental data** are used to determine model parameters.
  - HFF **additives** (including **persulfate**), different **SI** and **ionic strengths** are investigated.



# Quantitative prediction of celestite precipitation in hydraulic fracturing fluid systems

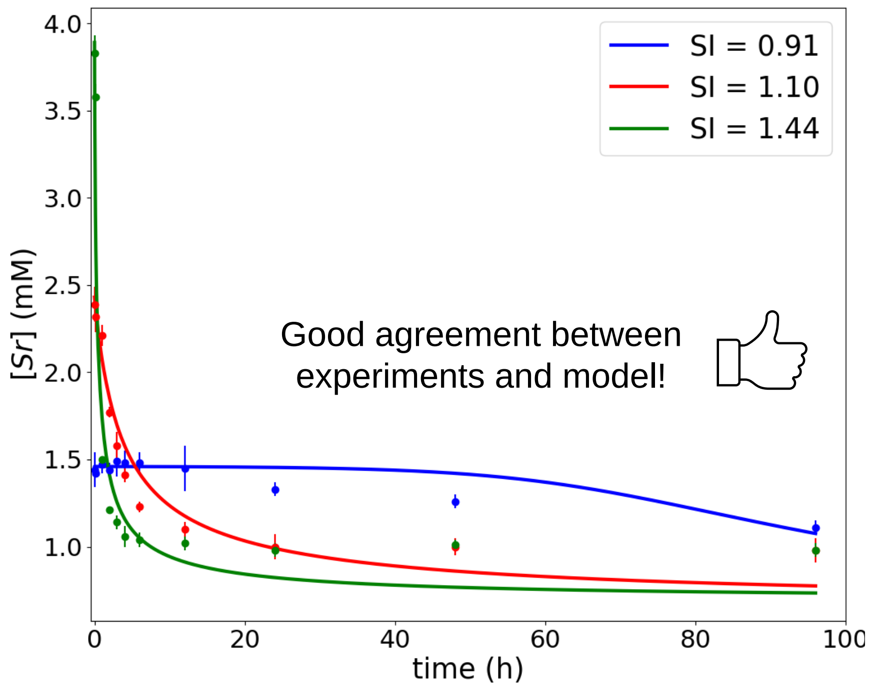
SLAC

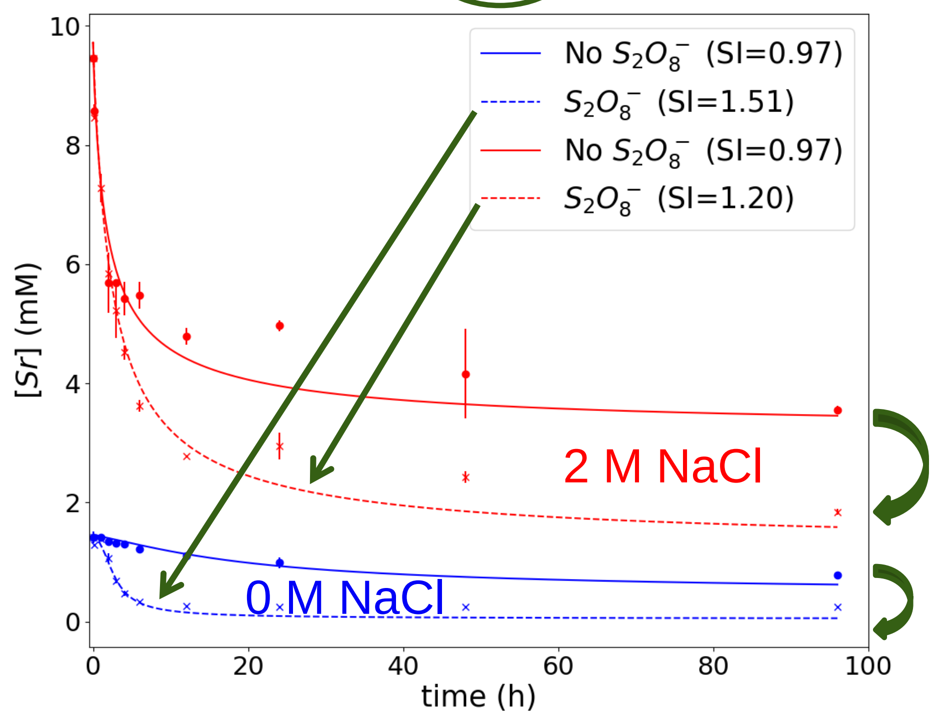
- Modeling results for celestite precipitation including persulfate.

Sr concentration decreases due to persulfate ability to drive more $SrSO_4$ formation

$$(NH_4)_2S_2O_8 \rightarrow 2NH_4^+ + S_2O_8^{2-}$$

$$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+ + \frac{1}{2}O_2$$

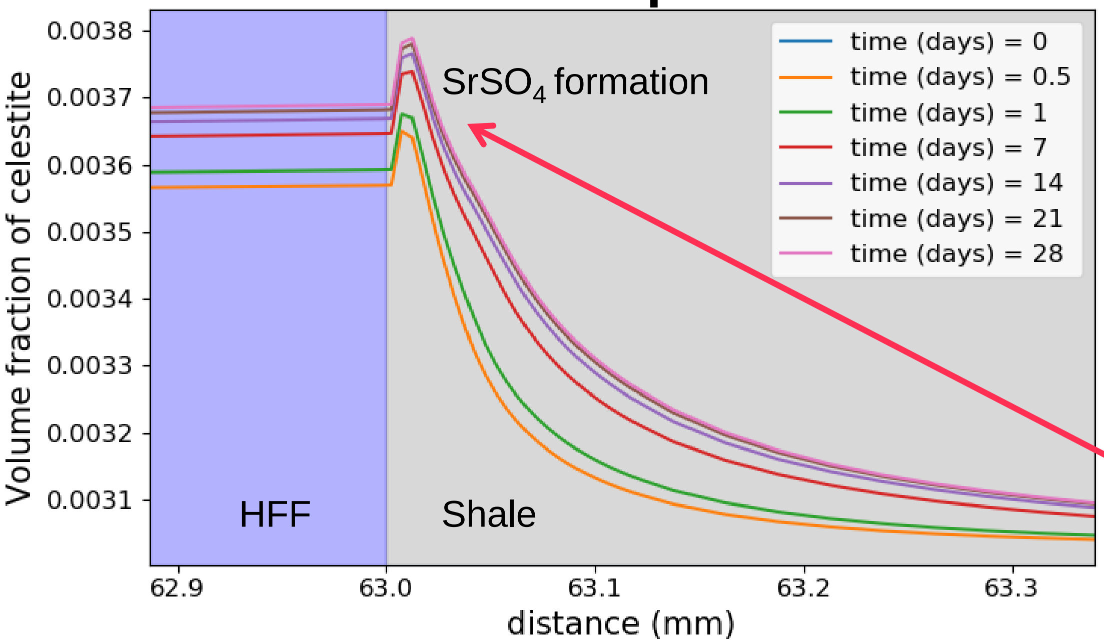


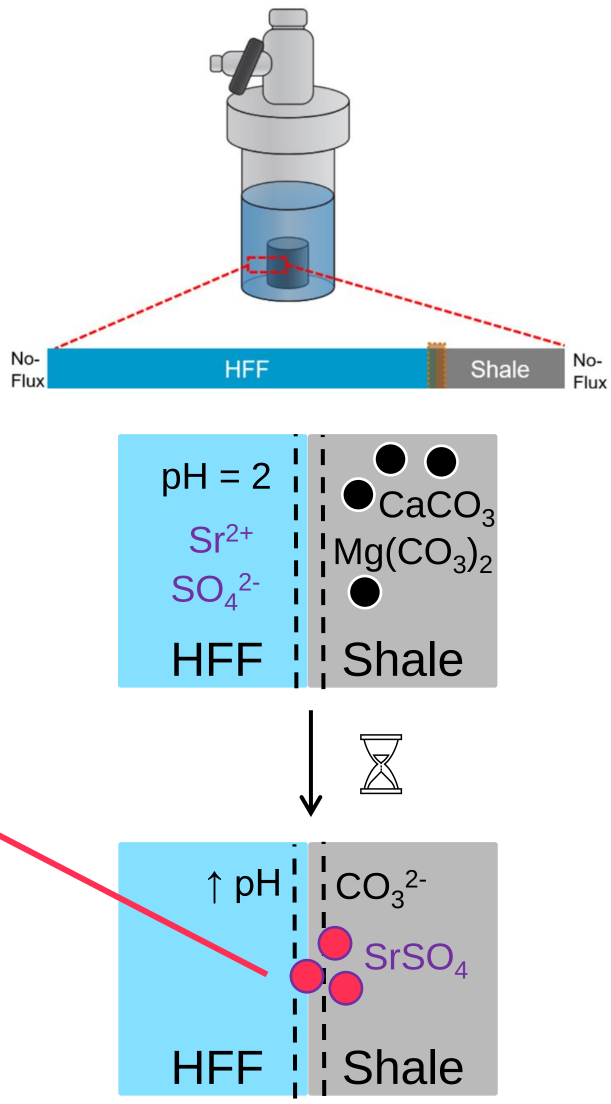




The curves illustrate the consumption of strontium due to celestite precipitation as a function of time. The points represent experimental results with their respective standard deviation and the lines are modeling results. Different colors are related to different saturation indexes.

# Quantitative prediction of celestite precipitation in hydraulic fracturing fluid systems

- Celestite precipitation in a shale system.
  - Promoted at near-neutral pH.
  - Carbonate dissolution neutralizes pH
  - **Celestite formation and carbonate dissolution are coupled**



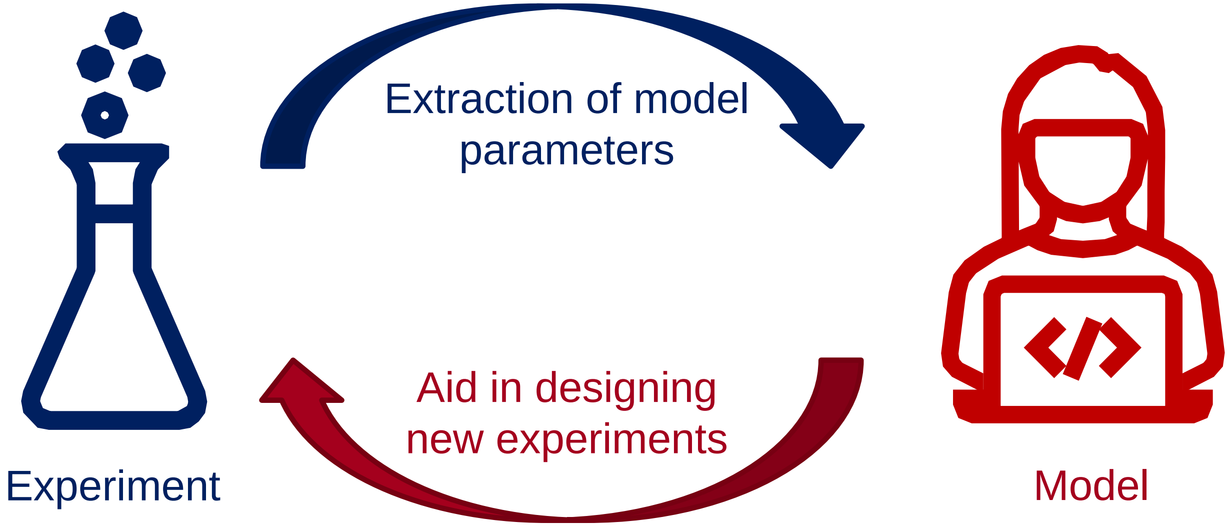




The curves present the volume fraction of celestite for different locations of the system. Celestite formation presents a peak near the interface where carbonates are mostly dissolved, and the pH increased.

# Quantitative prediction of celestite precipitation in hydraulic fracturing fluid systems

- **Kinetic and thermodynamic parameters** were determined for celestite precipitation with the aid of experimental data.
- The geochemical model quantifies **the location and extent** of celestite precipitation in a shale system.

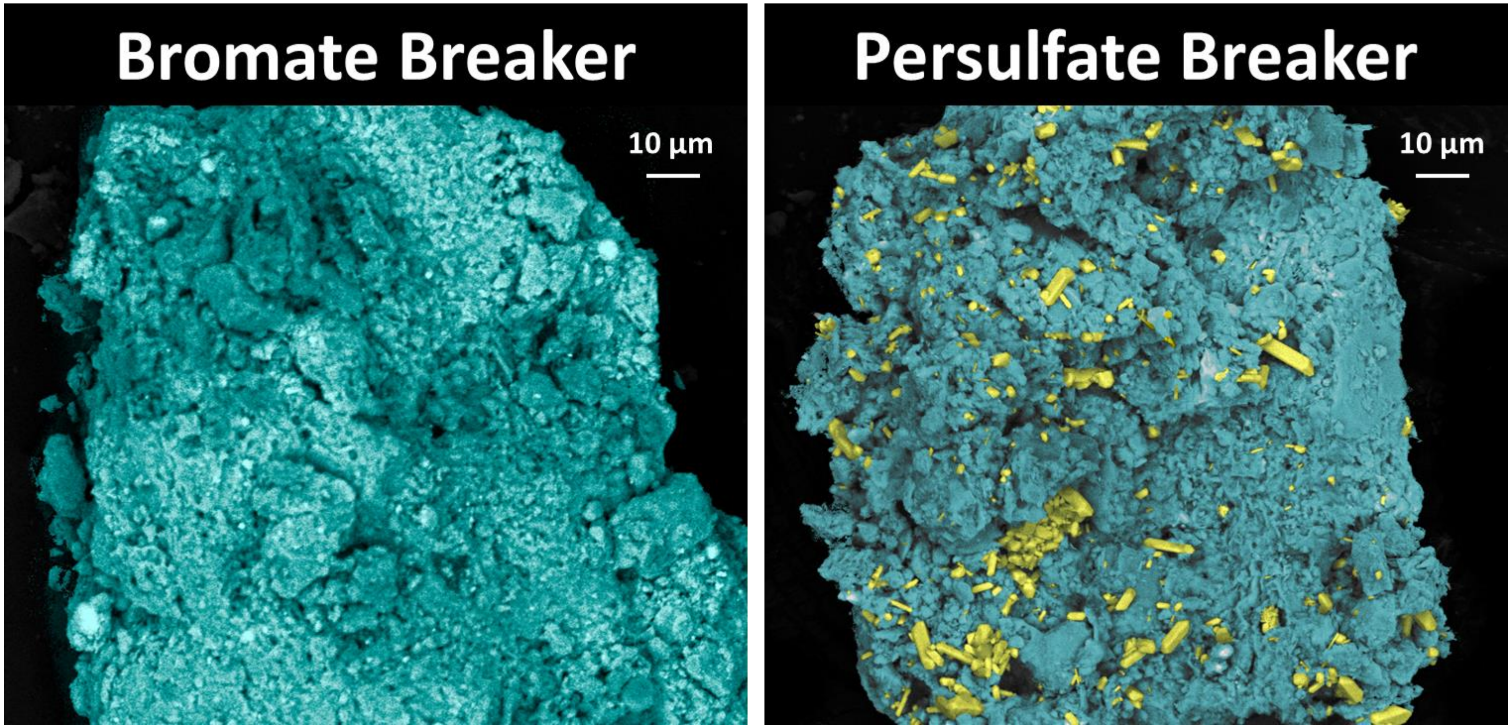
The global geochemical model for celestite precipitation developed under various synthetic hydraulic fracturing fluid conditions will contribute to constraining the chemical compositions of fluid necessary to mitigate strontium sulfate scale formation.



# Putting Knowledge to Use



- How does swapping persulfate breaker for bromate breaker affect sulfate scaling?
- Can breaker swap allow clean brines to be used as base fluids?




Secondary mineral precipitation (Celestite) identified in yellow

# Rock Physics for Monitoring Flow Pathways

CHARACTERIZATION: mineral scale, permeability

MODELING: simulated transport, reactions

Optimize POROSITY

Rock physics

MODELING: test new fluid compositions

EXPERIMENT: assess fluid compositions

Verify & optimize

Industry & research community

Can we monitor *effective* flow pathways using seismic?

Vanorio

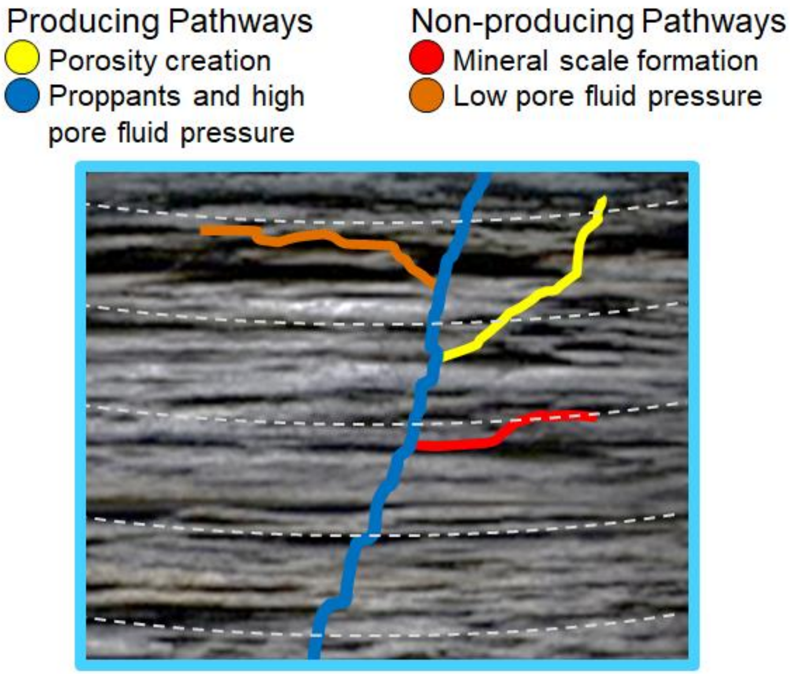
Ding

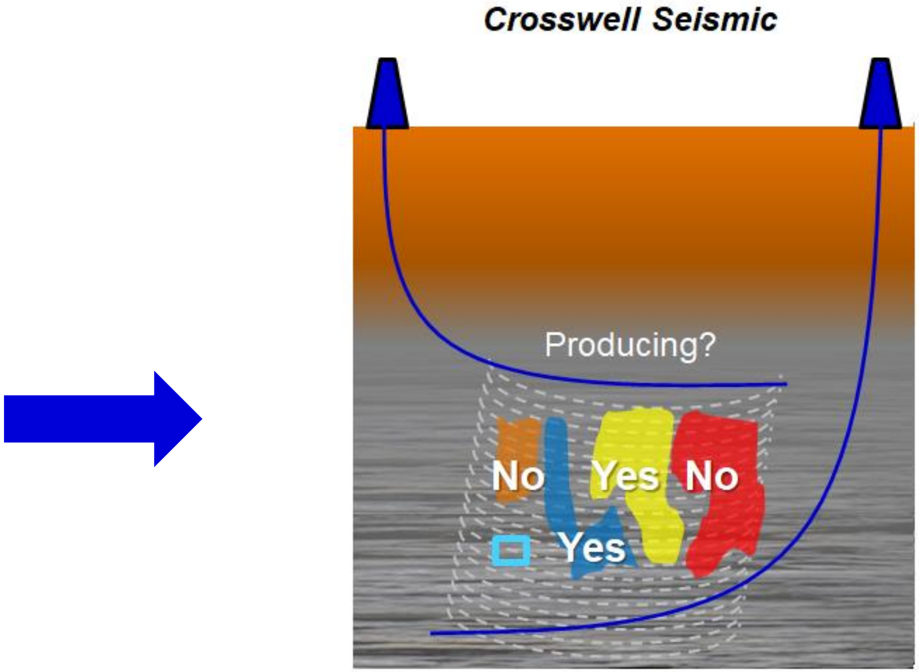
Clark

Stanford Geophysics

# Fracture Detection and Quantification

SLAC




- Fractures provide **primary producing pathways** for unconventional reservoirs.
- Hydro-Fracturing induces **chemical and mechanical alterations**.
- **Fracture properties** (e.g., orientation, geometry) significantly impact **fluid flow**.

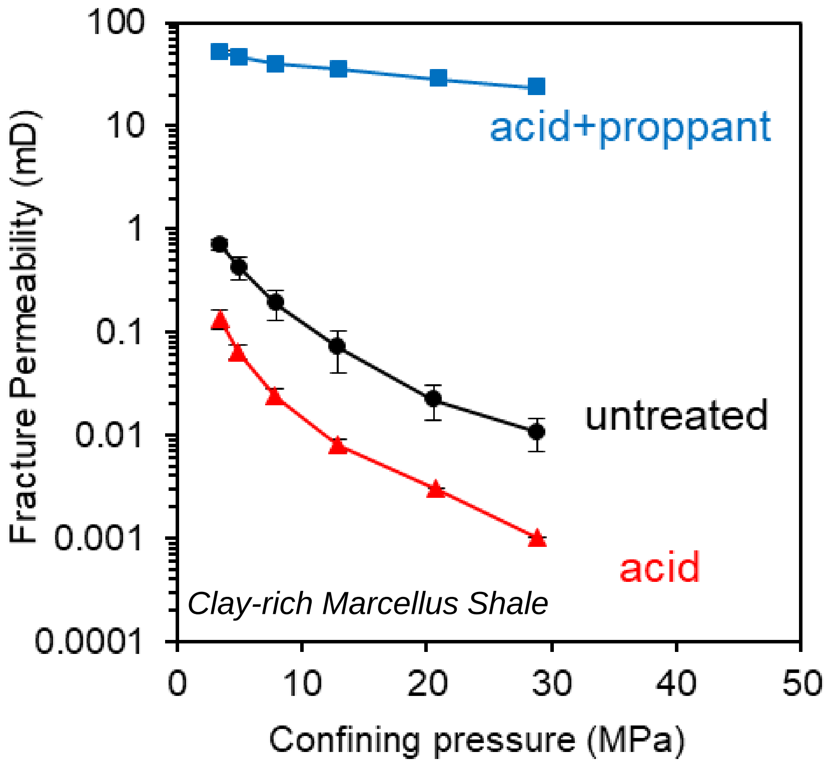
**Can producing pathways be detected seismically?**

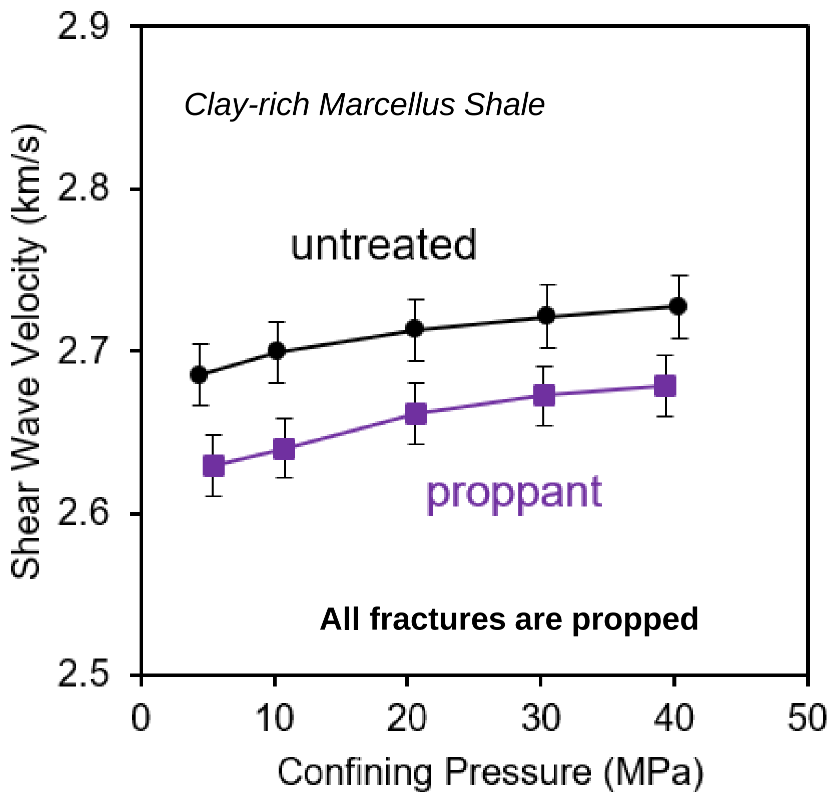
**Can fracture properties be quantified effectively?**

# Velocity Signatures of Producing Pathways

SLAC

- **Fracture permeability**
  - Reduced by acid treatment
  - Recovered and enhanced by proppant
- **Fracture detection capability**
  - Enhanced after acid treatment
  - Reduced for proppant in acidized fractures

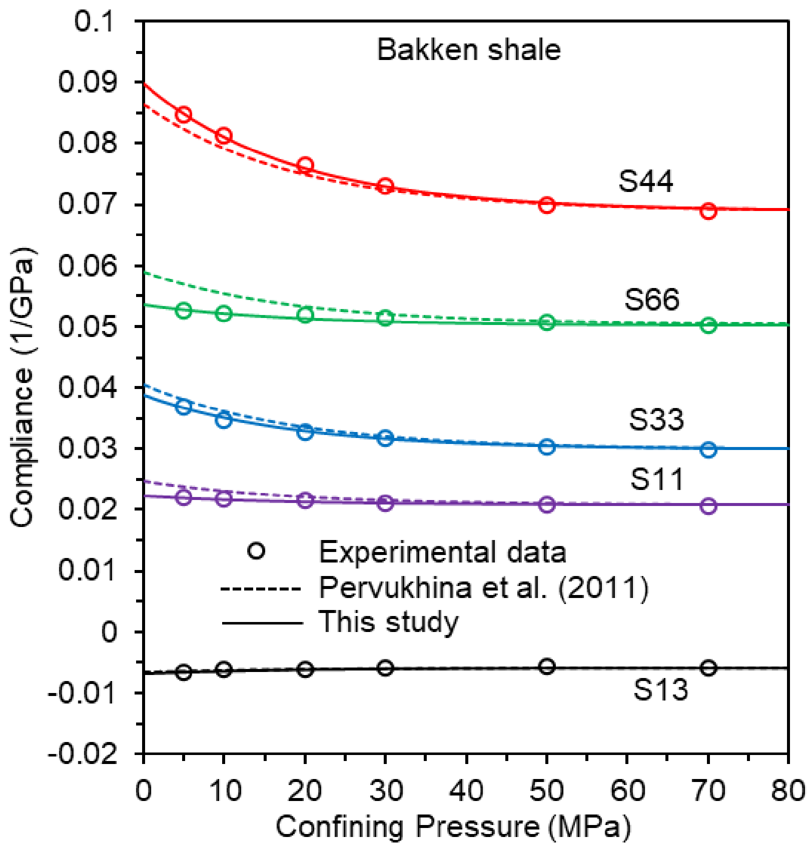


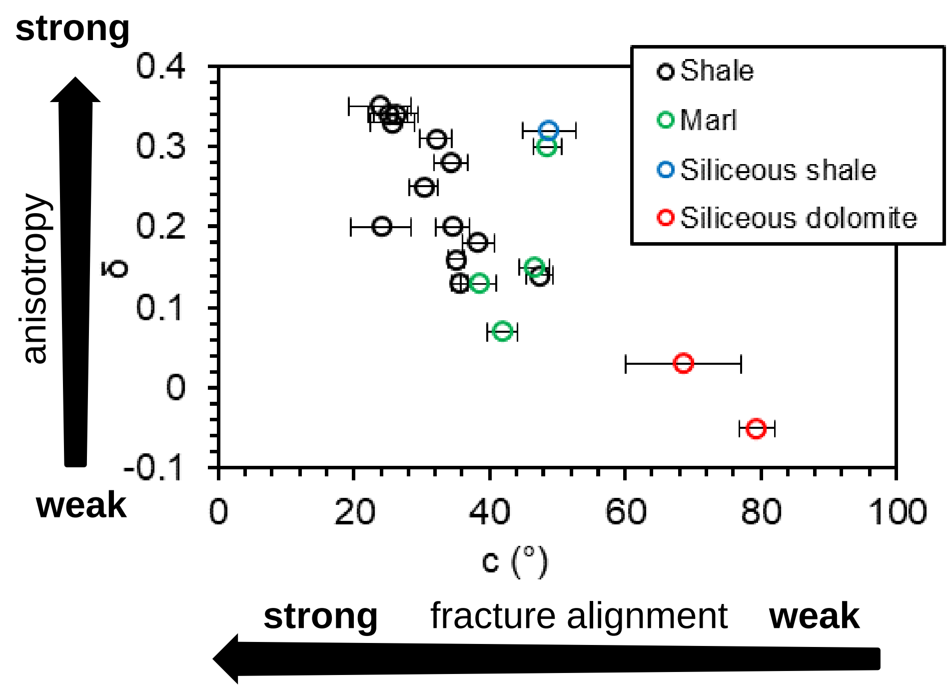




**Fractures can be seismically detected only when efficiently propped.**

# Fracture Alignment and Anisotropy

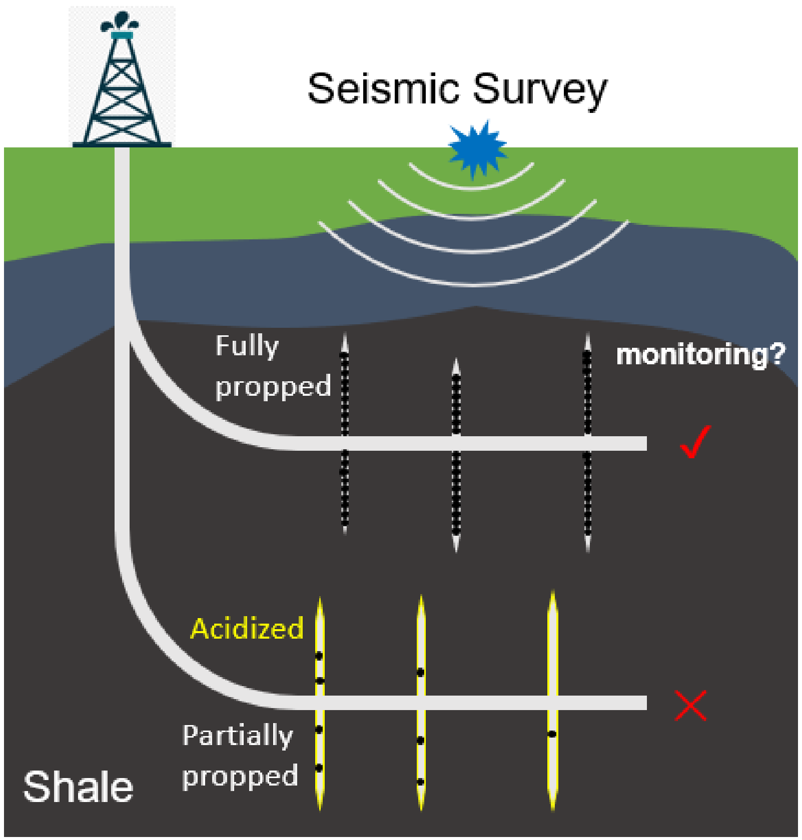
- **New rock physics model**
  - Implements a flexible function with variable width and amplitude
  - Enhances physical representation of fracture orientation distribution
  - Fully captures fracture alignment to bedding that impacts velocity anisotropy



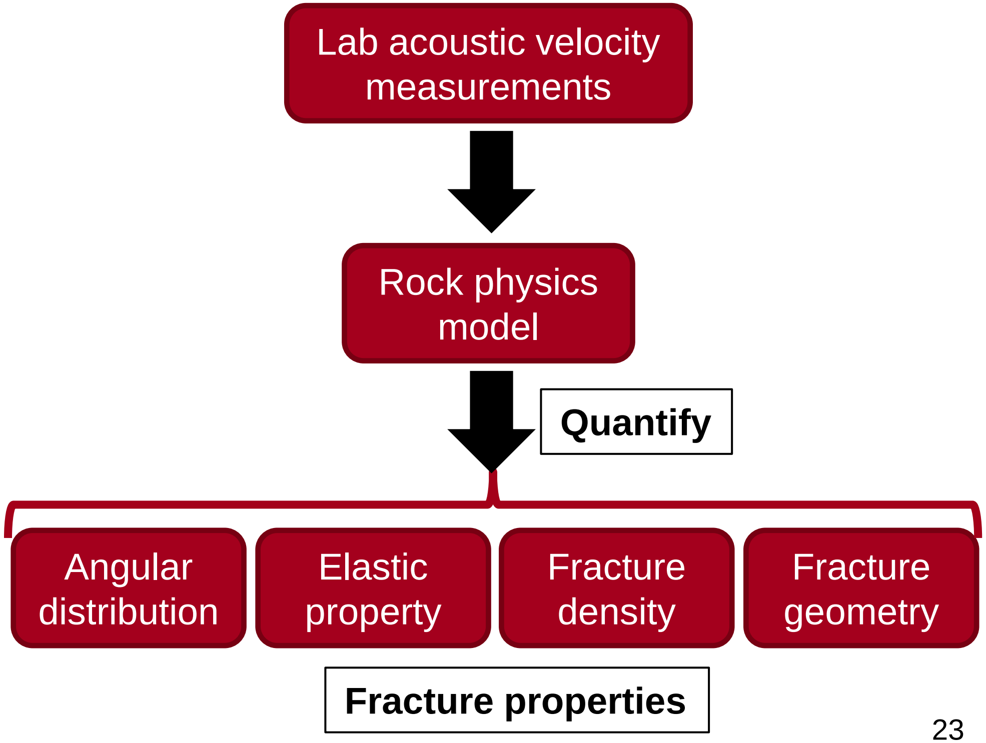



# Summary: the Role of Rock Physics

- **Fracture detection**
  - Fracture acidizing of clay-rich shale inhibits both flow and detection.
  - High propping efficiency allows the detection of producing pathways.




- **Fracture quantification**
  - The new Rock Physics model enhances the extraction of fracture orientation.
  - The new model is a useful tool for quantifying fracture properties.



# Manipulate porosity

SLAC

CHARACTERIZATION: mineral scale, permeability

MODELING: simulated transport, reactions

Optimize POROSITY

Rock physics

MODELING: test new fluid compositions

EXPERIMENT: assess fluid compositions

Verify & optimize

**Can we manipulate porosity to improve flow through fracture faces?**

Gundogar

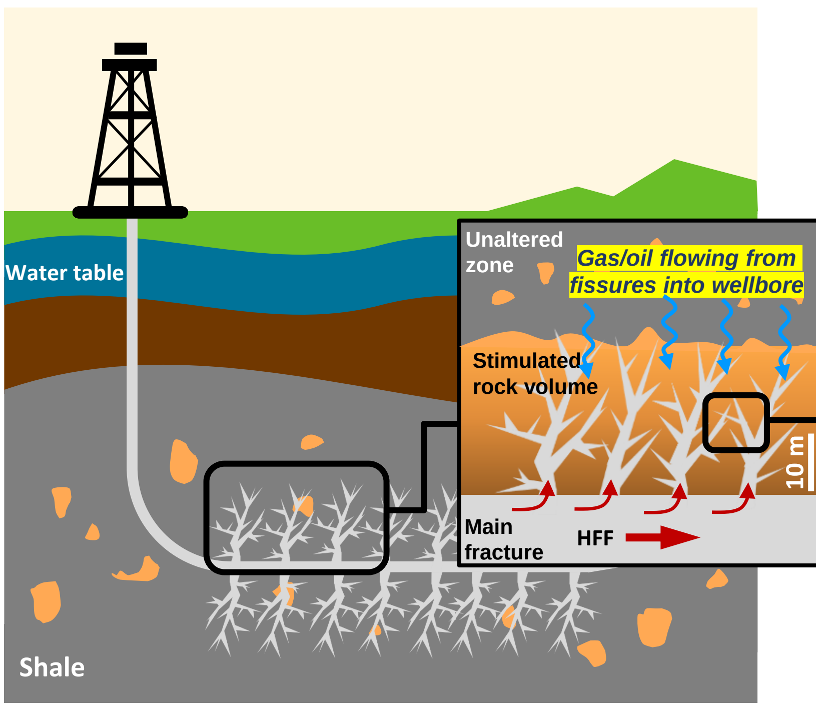
Kovscek

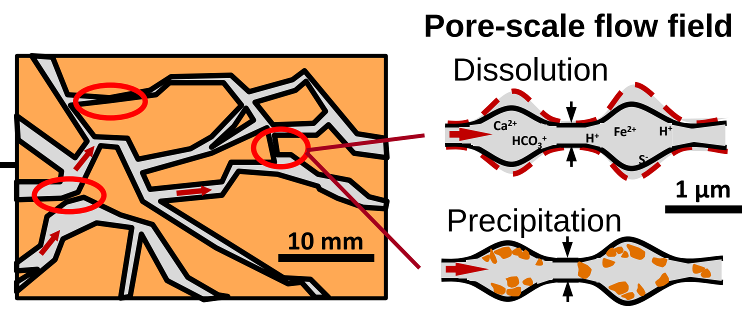
Industry & research community

# Task 3. Context

*The problem*: Injection conditions are far from optimal for stimulating matrix production

- size of acid slug
- pH
- salinity
- far from equilibrium wrt brine composition
- promotes scale formation



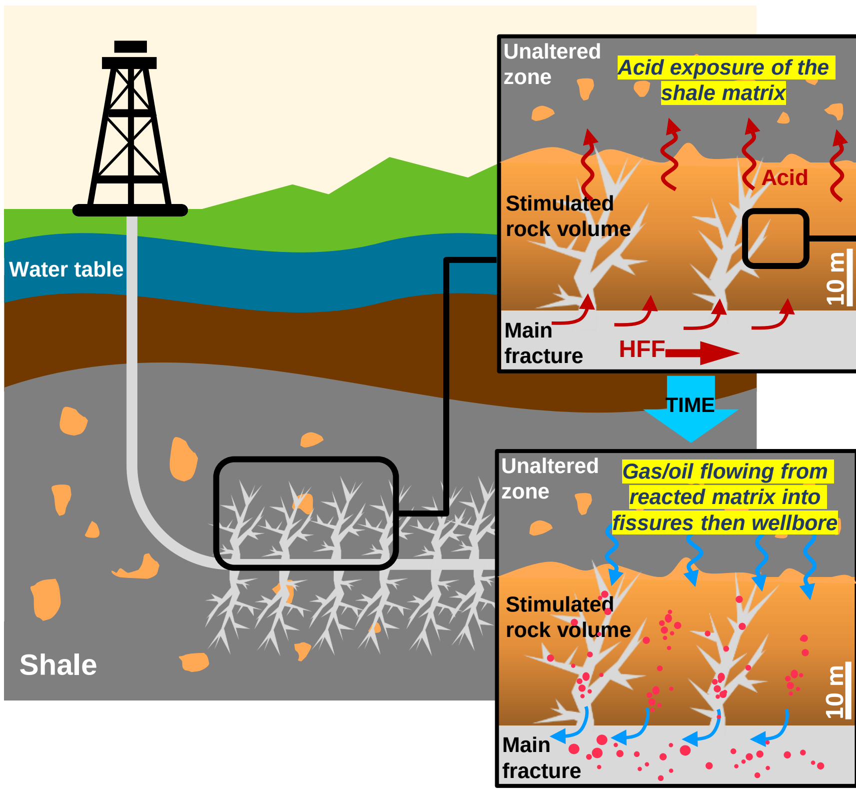

**Dissolution > Precipitation**
→ Enlarge existing channels and create newly merged pores
→ Improve interconnected porosity for enhanced contact with the matrix

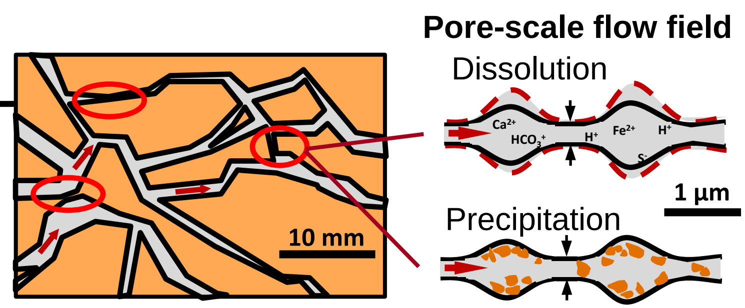
**Precipitation > Dissolution**
→ Narrow down cracks due to thickening of crack faces or total blocking of pores
→ Inhibit gas/oil flow out of matrix

# Task 3. Context

*The solution*: Manipulate chemistry and pressure to

- investigate reactions while transport is occurring
- understand conditions leading to scaling
- translate lab results to field conditions




**Dissolution > Precipitation**

→ Enlarge existing channels and create newly merged pores

→ Improve in interconnected porosity for enhanced contact with the matrix

**Precipitation > Dissolution**

→ Narrow down cracks due to thickening of crack faces or total blocking of pores

→ Inhibit gas/oil flow out of matrix

# Results: Core-flood permeability decreases w/porosity

## Core-scale measurements

| Sample | Method | Core porosity (vol.%) | |
|---|---|---|---|
| | | *Unreacted* | *Reacted* |
| Marcellus outcrop | Kr-filled CT fluid substitution | **3.1** | **1.9** |
| MSEEL carbonate-rich | | **2.9** | **2.1** |
| MSEEL clay-rich | He pulse-decay* | **10.2** | **5.7** |

***Marcellus outcrop***

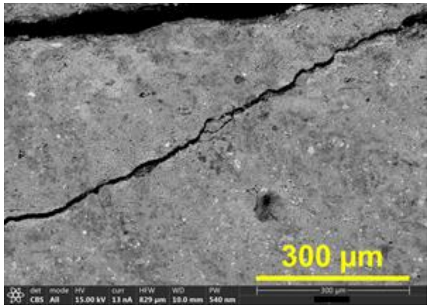
***MSEEL carbonate-rich (7556-7557')***

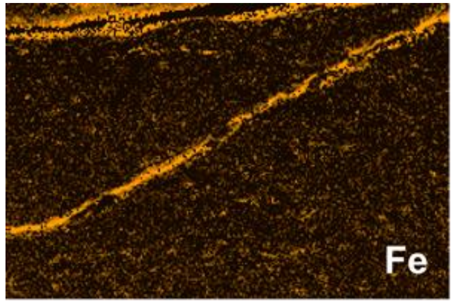
***MSEEL clay-rich (7536-7537')***

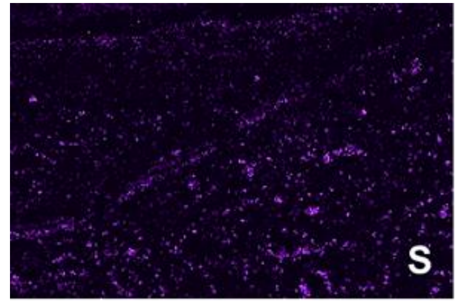
| Sample | Duration (days) | | Injected volume (PV) | | Core permeability (μD) | |
|---|---|---|---|---|---|---|
| | *Brine* | *Reactive fluid* | *Brine* | *Reactive fluid* | *Brine* | *Reactive fluid* |
| Marcellus outcrop | 7 | 16 | 13 | 6 | **7.2** | **1.2** |
| MSEEL carbonate-rich | 5 | 11 | 42 | 36 | **58** | **24** |
| MSEEL clay-rich | 8 | 14 | 31 | 18 | **10.3** | **2.2** |

# Results: Porosity decreases due to scaling and compaction

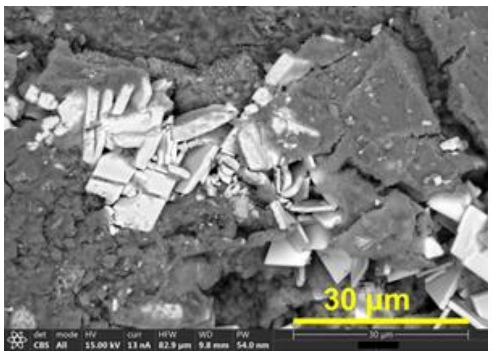
Pyrite dissolution + oxygen = abundant iron hydroxide precipitation via SEM/EDS

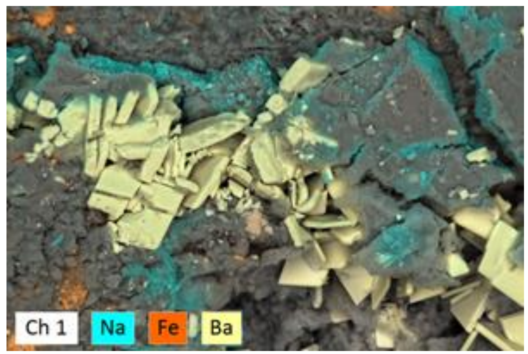


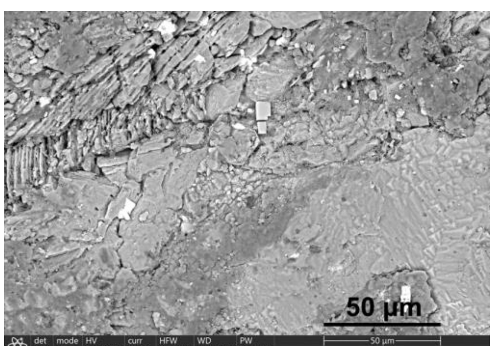



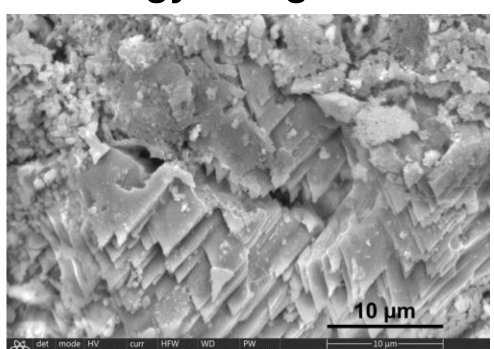

Barium ions + sulfate from breaker = abundant barite precipitation via SEM/EDS



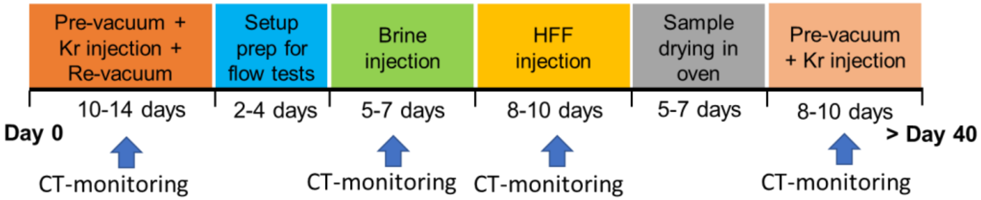

Acid + carbonate-rich mineralogy = significant dissolution via SEM/EDS



# Take-home messages

- Reactive flow-through experiments – an important complement to generate compositional data coupled with geochemical and geophysical changes in  reacted shales
- But, time consuming ->




- Shales are among the most reactive surfaces in the Earth's crust
- Reactivity of the abundant minerals determines the reaction extent
- To reduce scaling, adjust injected fluid chemistry to be compatible with the resident brine and mineral compositions, especially Fe in pyrite-rich shales
- Much more intense barite precipitation in the reacted MSEEL clay-rich sample compared to the carbonate-rich due to its greater amounts of pyrite, OM, clay minerals, and its fissile nature with multiple native cracks

# Major Findings

- Shales are highly reactive and mineral scaling occurs in all rocks regardless of different base fluids used
- Unequilibrated solutions negatively impact permeability
- Mineral scaling reduces porosity/permeability
- Additive degradation enhances sulfate scaling
- Changing additives rather than further cleaning clean brines is most cost effective strategy
- Geochemical modeling streamlines laboratory testing of new formulations
- Rock physics modeling provides fracture orientation distribution which allows more information to be derived from seismic data

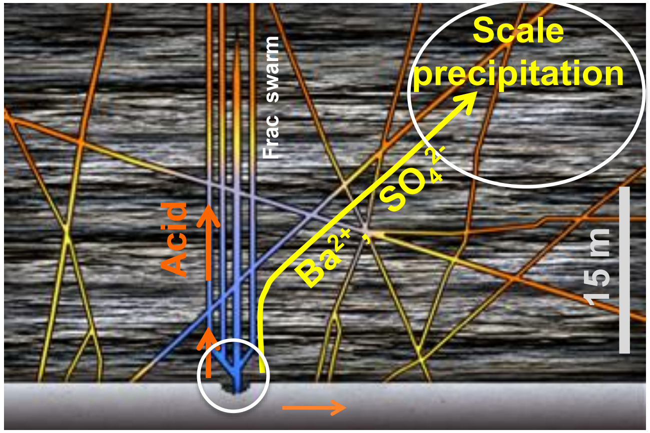
# Project Management slides

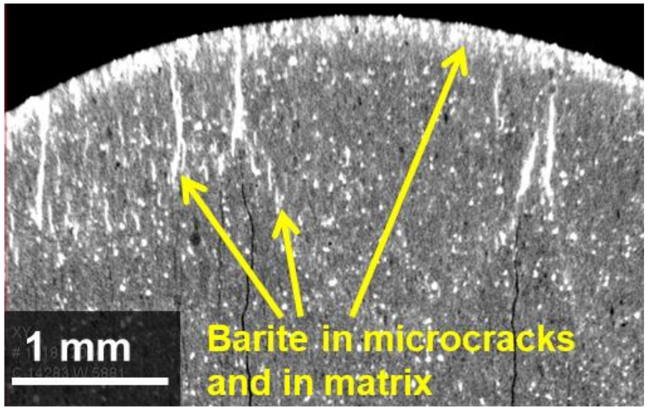
# Accomplishments



**Accomplishments:**

- ✓ Published 26 manuscripts; 2 in review; 3 in preparation: Fe, Ba, and Sr scale formation mechanisms
- ✓ Developed & patented acid-swap mitigation for Ba scale
- ✓ Identified additive degradation as primary cause of sulfate scaling
- ✓ Working with 3 industrial partners to use new scale mitigation knowledge in industrial practices
- ✓ Able to use geochemical modeling to anticipate scaling in complex systems
- ✓ Introduced new technologies for unconventional geochemistry monitoring and modeling to maximize data analysis



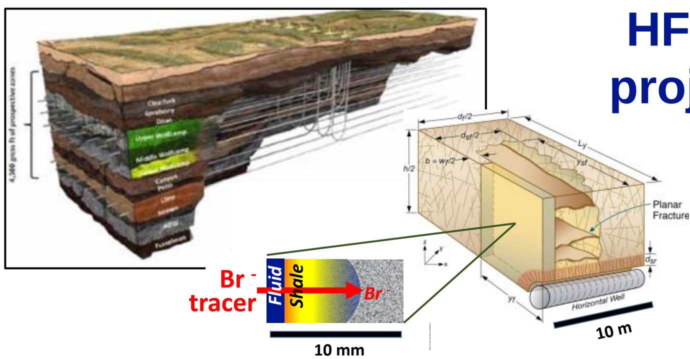



# Lessons learned

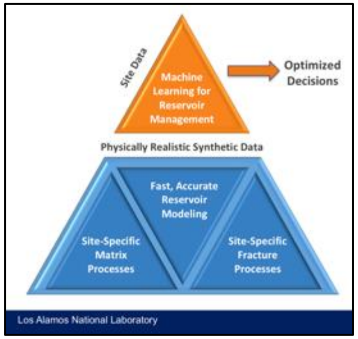
- Modeling is crucial to testing process models and finding weaknesses in understanding of shale geochemistry
- Unintended consequences of additives use can have a significant impact on mineral scaling
- Comparing shale-fluid reactivity across basins, compositions is critical to developing geochemical and geomechanical insights (universal vs. play specific problems)
- Laboratory-based surface imaging techniques (SEM) can not be used to study reactions/precipitation occurring in shale matrix but do compliment other techniques

# Synergies & Opportunities

## National Laboratory Partners




**HFTS project**




Unconventional Reservoir Management

## Industrial Partners

# Project Summary

https://netl.doe.gov/node/6301:

This project is focusing on two strategic geochemistry-based research thrusts where new knowledge can immediately begin to improve unconventional gas and oil recovery factors. First, we are evaluating mineral scale precipitation processes specific to major shale formations and fracture stimulation practices and developing geochemistry-based approaches to mitigate it. This knowledge has an additional benefit of improving our ability to reuse flowback and produced water without causing formation damage. The focus of this work will be to compare and contrast conditions specific to Marcellus (dry gas) and Midland (oil) basins. We are also conducting research to understand how geochemistry can be used to manipulate the thickness and permeability of the altered zone by focusing on controlling microscale chemical and mechanical features such as secondary porosity created during stimulation, the connectivity of this porosity across the altered zone, and irreversible mineral scale precipitation within the altered zone. Our ultimate goal is to develop approaches to manipulate the thickness and permeability of the altered zone during stimulation to increase access to matrix and thus production recovery factors.

To monitor scale precipitation and microstructure evolution within shales, we are using a combination of laboratory, synchrotron X-ray imaging, computed tomography, electron microscopy, and seismic techniques. Research is being performed in consultation with industrial experts to help facilitate technology transfer from the laboratory to the field.

## Next steps:

- Develop mitigation strategies

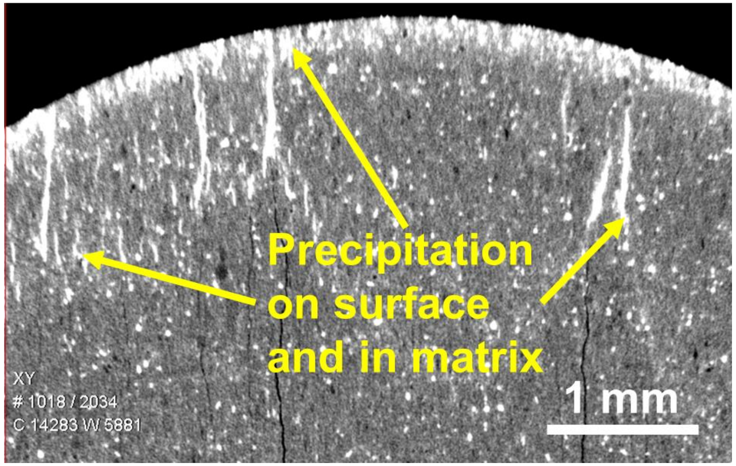
# Appendices

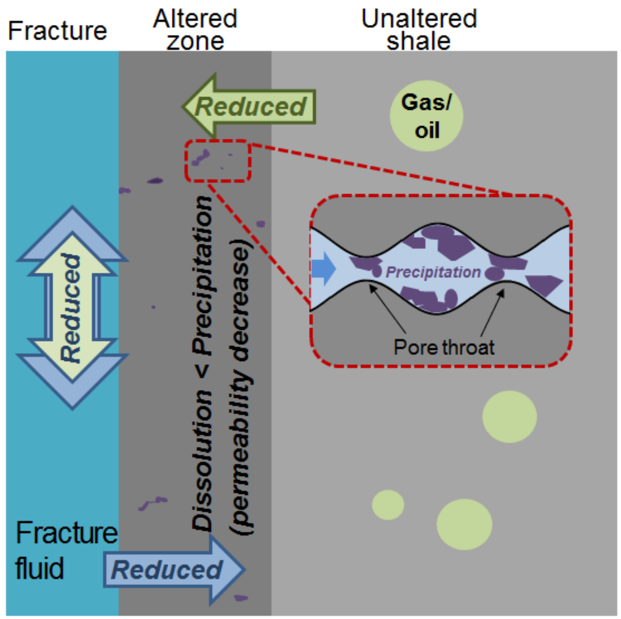
# Benefit to the Program

**Program goals addressed:**

- Improve ***recovery factors***
- Design better additive mixtures
- Improve ***water reuse/recycling***
- Provide new knowledge for geochemical control of subsurface mineral scale and porosity

***Fracture-fluid interfaces are crucial***



# Project overview

**Project goals:** Develop new knowledge about critical mineral scale and porosity generating processes. Use this information enable transformation industrial processes to IMPROVE EFFICIENCY and WATER REUSE

(i) Identify chemical parameters that control scale in different basins.

(ii) Develop chemical strategies to mitigate scale.

(iii) Develop next-generation geochemistry tools to monitor & mitigate subsurface mineral scale precipitation and optimize porosity *in real time in the field*

(iv) Systematically manipulate altered zone porosity to improve permeability

**Success criteria:**

- On-time execution of PMP
- Presentations at industrial and scientific meetings
- Publications in major journals, including URTeC proceedings
- Interaction with industry
- Patent filings

# Organization Chart, Expertise, and Roles

**SLAC director**
Chi-Chang Kao

**SSRL director**
Paul McIntyre

**SSRL science director**
Britt Hedman

**Senior Scientist, Research Manager**
John Bargar

*Background: Geochemistry synchrotron-based spectroscopy, imaging*

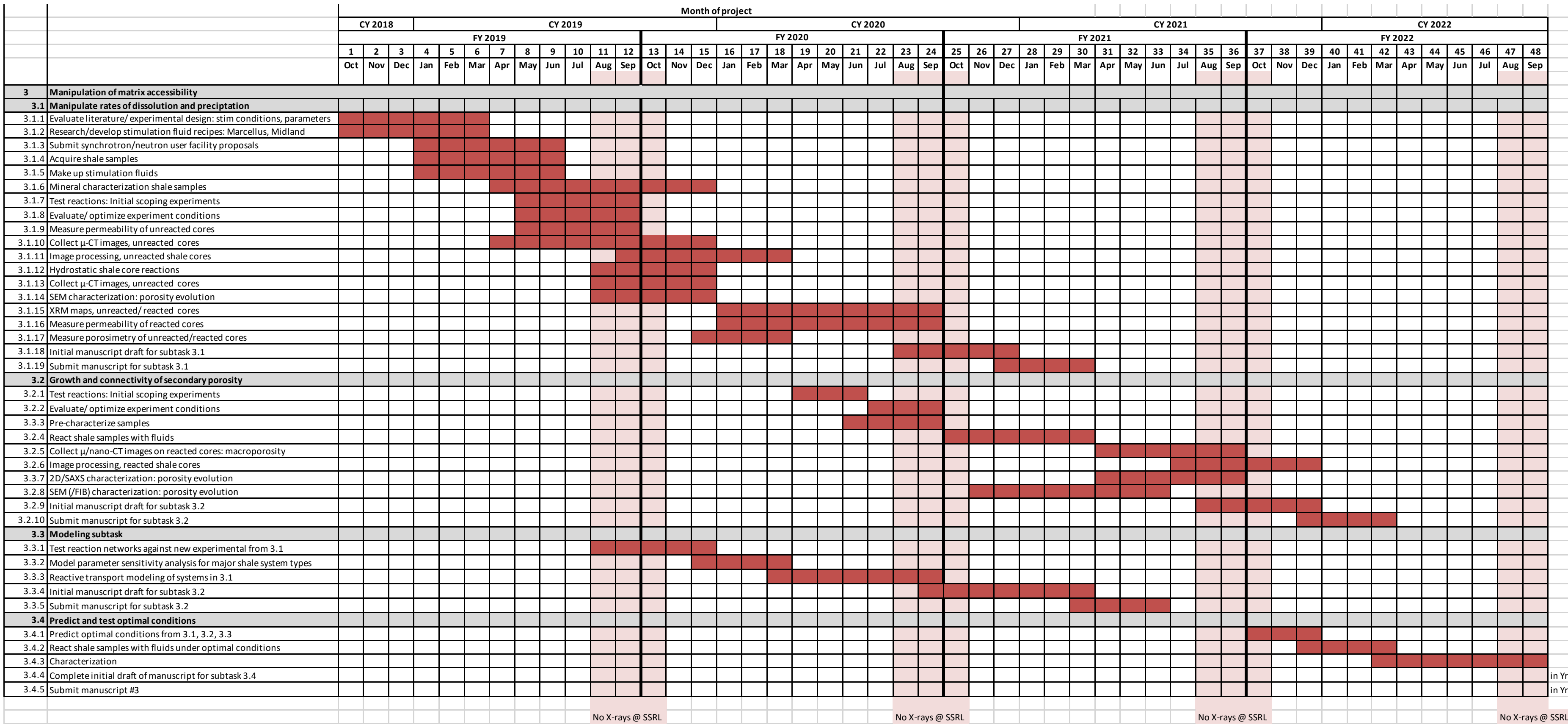
| | Task lead | Postdoctoral scholar |
|---|---|---|
| **Task 1.0:** | John Bargar | Program management |
| **Task 2.1:** | Adam Jew<br>*Geochemistry* | Eleanor Spielman-Sun |
| **Task 2.2:** | Jennifer Druhan<br>*Reactive transport* | Qingyun Li,<br>Barbara de Farias Esteves |
| **Task 2.3:** | Tiziana Vanorio<br>*Rock physics* | Jihui Ding |
| **Task 3.0:** | Tony Kovscek:<br>*Fluid flow, reservoir engineering* | Asli Gundogar |

# Gantt Chart: Tasks 1-2

SLAC

| Task | Title | Month of project (shaded months) | |
|---|---|---|---|
| 1 | **Task 1. Project management** | | |
| 1.1 | Development/Refinement of PMP | 20, 21, 22 | |
| 1.2 | Quarterly research performance reports | 4, 7, 10, 16, 19, 22, 28, 31, 34, 40, 43, 46 | |
| 1.3 | Meetings with NETL research groups | 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 36, 39, 42, 45, 48 | |
| 1.4 | Annual research performance report | 14, 26, 38 | |
| 1.5 | Final technical report | 48 | |
| 2 | **Task 2. Scale prediction and mitigation in the stimulated rock volume** | | |
| 2.1 | **Prediction of mineral scaling in unconventional reservoirs** | | |
| 2.1.1 | **Experimental subtask** | | |
| 2.1.1.1 | Evaluate literature/ experimental design | 1–6 | |
| 2.1.1.2 | Complete initial scoping experiments | 4–6 | |
| 2.1.1.3 | React shale with fracture fluid | 5–12 | |
| 2.1.1.4 | Characterize post-reaction shale samples: laboratory-based methods | 9–15 | |
| 2.1.1.5 | Analyze solution data from reactor experiments | 9–15 | |
| 2.1.1.6 | Characterize precipitates: sychrotron-based methods | 14–21 | |
| 2.1.1.7 | Initial manuscript draft for subtask 2.1.1 | 22–27 | |
| 2.1.1.8 | Submit manuscript for subtask 2.1.1 | 28–30 | |
| 2.1.2 | **Modeling subtask** | | |
| 2.1.2.1 | Develop model framework | 1–9 | |
| 2.1.2.2 | Test reaction networks against new experimental from 2.1.1 | 9–15 | |
| 2.1.2.3 | Model parameter sensitivity analysis for major shale system types | 13–18 | |
| 2.1.2.4 | Reactive transport modeling of systems in 2.1.1 | 17–24 | |
| 2.1.2.5 | Initial manuscript draft for subtask 2.1.2 | 25–30 | |
| 2.1.2.6 | Submit manuscript for subtask 2.1.2 | 30–33 | |
| 2.2 | **Mitigation of mineral scaling in unconventional reservoirs** | | |
| 2.2.1 | **Modeling task** | | |
| 2.2.1.1 | Conduct numerical optimizaiton experiments for each shale system | 28–33 | |
| 2.2.1.2 | Evaluate cost/availability of constituents of optimized parameters | 24–27 | |
| 2.2.1.3 | Develop experimental program based on optimizations | 28–30 | |
| 2.2.1.4 | Initial manuscript draft for subtasks 2.2.1.1-3 | 31–36 | |
| 2.2.1.5 | Submit manuscript for subtasks 2.2.1.1-3 | 37–39 | |
| 2.2.1.6 | Re-evaluate/refine model as experimental data become available | 40–45 | |
| 2.2.1.7 | Refine model-based experimental optimization procedure | 39–42 | |
| 2.2.1.8 | Initial manuscript draft for subtasks 2.2.1.6-7 | 42–45 | |
| 2.2.1.9 | Submit manuscript for subtasks 2.2.1.6-7 | 46–48 | |
| 2.2.2 | **Experimental task** | | |
| 2.2.2.1 | Formulation of new fracture fluid recipes | 9–20 | |
| 2.2.2.2 | Testing of new formulations for various scaling conditions w/out shale | 13–24 | |
| 2.2.2.3 | React shale with optimized fracture fluid | 23–27 | |
| 2.2.2.4 | Characterize post-reaction shale samples: laboratory-based methods (optimized fluids) | 28–33 | |
| 2.2.2.5 | Analyze solution data from reactor experiments (optimized fluids) | 28–33 | |
| 2.2.2.6 | Characterize precipitates: sychrotron-based methods (optimized | 30–36 | |
| 2.2.2.7 | Initial manuscript draft for subtask 2.2.1 | 35–39 | |
| 2.2.2.8 | Submit manuscript for subtask 2.2.1 | 39–42 | |
| 2.2.2.9 | Optimize/reformulate fluids | 30–36 | |
| 2.2.2.10 | Re-test new formulations (after reformulating) | 35–39 | in Yr 5 |
| 2.2.2.11 | Initial manuscript draft for Tasks 2.2.1.9-10 | 39–42 | in Yr 5 |
| 2.2.2.12 | Submit manuscript for Tasks 2.2.1.9-10 | 42–44 | in Yr 5 |
| 2.3 | **Acoustic Measurements on Laboratory reacted shales** | | |
| 2.3.1 | SEM images of top and bottom of unreacted shale | 3–6 | |
| 2.3.2 | Measurement of grain density, bulk density, and porosity (pre- | 6–12 | |
| 2.3.3 | React Shale samples with fracture fluid | 10–15 | |
| 2.3.4 | SEM images of top and bottom of reacted shale | 12–18 | |
| 2.3.5 | Measurement of grain density, bulk density, and porosity (post-reaction) | 17–24 | |
| 2.3.6 | Rock physics modeling | 19–27 | |
| 2.3.7 | Post-injection stress-strain-strength curve measurement | 24–34 | |
| 2.3.8 | Initial manuscript draft for subtask 2.3 | 33–39 | |
| 2.3.9 | Submit manuscript for subtask 2.3 | 39–42 | |

# Gantt Chart: Task 3



# Publications

SLAC

**Patents**

1. Patent (2019) - Fracture fluid alteration to mitigate barite scale precipitation in unconventional oil/gas shale systems. Patent ID: 62/717326

**Manuscripts published, submitted, or in revision**

2. Gundogar, A.S.; Ross, C.M.; Druhan, J.L., Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Transport-Related Consequences of Geochemical Interactions between Shale, Formation Brine, and Reactive Fluid. Accepted by InterPore2021 13th Annual Meeting.
3. Gundogar, A.S.; Druhan, J.L., Ross, C.M.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Core-flood Effluent and Shale Surface Chemistries in Predicting Interaction between Shale, Brine, and Reactive Fluid. Accepted by **2021** URTeC Annual Conference.
4. Jew, A.D.; Bargar, J.R.; Brownlow, J.W.; Laughland, M. Rethinking Mineral Scaling: What, Where, and Why is it occurring in the stimulated rock volume. Accepted by **2021** URTeC Annual Conference.
5. Spielman-Sun, E.; Jew, A.D.; Druhan, J.L.; Bargar, J.R. Controlling Strontium Scaling in the Permian Basin through Manipulation of Base Fluid Chemistry and Additives. Accepted by **2021** URTeC Annual Conference.
6. Ding, J.; Clark, A.C.; Vanorio, T.; Jew, A.J.; Bargar, J.R. Quantifying shale fracture properties from elastic stress sensitivity. Accepted by **2021** URTeC Annual Conference.
7. Ding, J.; Clark, A.C.; Vanorio, T.; Jew, A.J.; Bargar, J.R. Rock physics modeling of crack-induced stress sensitivity. Submitted to **2021** SEG Annual Conference.
8. Birkholzer, J. T.; Morris, J.; Bargar, J. R.; Brondolo, F.; Cihan, A.; Crandall, D.; Deng, H.; Fan, W.; Fu, W.; Fu, P.; Hakala, A.; Hao, Y.; Huang, J.; Jew, A. D.; Kneafsey, T.; Li, Z.; Lopano, C.; Moore, J.; Moridis, G.; Nakagawa, S.; Noël, V.; Reagan, M.; Sherman, C. S.; Settgast, R.; Steefel, C.; Voltolini, M.; Xiong, W.; Ciezobka, J. A new modeling framework for multi-scale simulation of hydraulic fracturing and production from unconventional reservoirs. *Energies*, 14 (3), 641, **2021.**

# Publications


9. Ding, J.; Clark, A.C.; Vanorio, T.; Jew, A.J.; Bargar, J.R. Acoustic velocity and permeability of acidized and propped fractures in shale, *Geophysics*. In revision, **2021**.
10. Gundogar, A.S.; Ross, C.M.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale investigation of geochemical alterations in marcellus shale through reactive core-floods, *Energy & Fuels*. In revision, **2021**.
11. Li, Q.; Wang, L.; Perzan, Z.; Caers, J.; Brown, G.E. Jr.; Bargar, J.R.; Maher, K. Global Sensitivity Analysis of a Reactive Transport Model for Mineral Scale Formation During Hydraulic Fracturing" was published in Environmental Engineering Science, 38(3), **2021**, https://doi.org/10.1089/ees.2020.0365.
12. Jew, A. D.; Bargar, J. R.; Brownlow, J., Strontium behavior in midland basin unconventional reservoirs: the importance of base fluids. *Extended abstract of the Unconventional Resources Technology Conference: Jul 19-22, Austin, TX*, **2020**.
13. Jew, A. D.; Besancon, C. J.; Roycroft, S. J.; Noel, V. S.; Brown, G. E. Jr.; Bargar, J. R., Chemical speciation and stability of uranium in unconventional shales: impact of hydraulic fracture fluid. *Environmental Science and Technology*, 54 (12) 7025-7734, **2020.**
14. Li, Q.; Jew, A. D.; Brown, G. E. Jr.; Bargar, J. R.; Maher, K., Reactive transport modeling of shale-fluid interactions after imbibition of fracturing fluids. *Energy and Fuels*, 34 (5), 5511-5523, **2020**.
15. Ding, J.; Clark, A. C.; Vanorio, T.; Jew, A. D.; Bargar, J. R., Acoustic velocity signatures of acidized and propped fractures in Marcellus shale. *SEG conference*. Accepted, **2020**.
16. Gundogar, A. S.; Ross, C. M.; Li, Q.; Jew, A. D.; Bargar, J. R.; Kovscek, A. R., Multiscale imaging of core flooding experiments during transport of reactive fluids in fractured unconventional shales. *Extended abstract for the 2020 SPE Western Regional Meeting*, *Bakersfield, CA, April 27–30*. Accepted and decided to postpone to a later date, **2020**.

# Publications


17. Ding, J.; Clark, A. C.; Vanorio, T.; Jew, A. D.; Bargar, J. R., Time-lapse acoustic monitoring of fracture alteration in Marcellus shale. *Extended abstract of the Unconventional Resources Technology Conference: Jul 19-22, Austin, TX*, **2020**.
18. Ding, J.; Mighani, S.; Clark, A. C.; Vanorio, T., Monitoring chemo-mechanical fracture behavior through engineering geophysics experiments. *Extended abstract for the 82nd EAGE Conference & Exhibition 2020, June 8-11, 2020, Amsterdam, Netherlands*. Accepted and rescheduled to December 10, **2020**.
19. Jew, A. D.; Li, Q.; Cercone, D.; Brown, G.E. Jr.; Bargar, J. R., A new approach to controlling barite scaling in unconventional systems. URTEC-512-MS. *Extended Abstracts of the Unconventional Resources Technology Conference*: *Denver, Colorado, USA* **2019**. DOI 10.15530/urtec-2019-512.
20. Li, Q.; Jew, A. D.; Kohli, A.; Maher, K.; Brown, G. E. Jr.; Bargar, J. R., Thicknesses of chemically altered zones in shale matrices resulting from Interactions with hydraulic fracturing fluid. *Energy & Fuels* **2019**, 33 (8), 6878-6889. DOI: 10.1021/acs.energyfuels.8b04527
21. Li, Q.; Jew, A.; Cercone, D.; Bargar, J.; Brown, G. E. Jr.; Maher, K., Geochemical modeling of iron (hydr)oxide scale formation during hydraulic fracturing operations. *Extended Abstracts of the Unconventional Resources Technology Conference: Denver, Colorado, USA* **2019**, p 14. DOI: 10.15530/urtec-2019-612.
22. Jew, A. D.; Li, Q.; Cercone, D.; Maher, K.; Brown, G. E. Jr.; Bargar, J. R., Barium sources in hydraulic fracturing systems and chemical controls on its release into solution. *Extended Abstracts of the Unconventional Resources Technology Conference: Houston, Texas, USA* **2018**, p 12. DOI: 10.15530/URTEC-2018-2899671.
23. Li, Q.; Jew, A. D.; Kiss, A. M.; Kohli, A.; Alalli, A.; Kovscek, A. R.; Zoback, M. D.; Cercone, D.; Maher, K.; Brown, G. E., Jr.; Bargar, J. R., Imaging pyrite oxidation and barite precipitation in gas and oil shales. *Extended Abstracts of the Unconventional Resources Technology Conference: Houston, Texas, USA* **2018**, p 10. DOI: 10.15530/URTEC-2018-2902747.

# Publications

SLAC


24. Alalli, A.; Li, Q.; Jew, A.; Kohli, A.; Bargar, J.; Zoback, M.; Kovscek, A., Effects of hydraulic fracturing fluid chemistry on shale matrix permeability. *Extended Abstracts of the Unconventional Resources Technology Conference: Houston, Texas, USA* **2018**, p 10. DOI: 10.15530/URTEC-2018-2881314.
25. Dustin, M. K.; Bargar, J. R.; Jew, A. D.; Harrison, A. L.; Joe-Wong, C.; Thomas, D. L.; Brown, G. E.Jr.; Maher, K., Shale kerogen: hydraulic fracturing fluid interactions and contaminant release. *Energy & Fuels* **2018**, 32 (9), 8966-8977. DOI: 10.1021/acs.energyfuels.8b01037.
26. Jew, A. D.; Harrison, A. L.; Kiss, A. M.; Dustin, M. K.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown, G. E. Jr.; Cercone, D.; Bargar, J. R., Mineralogical and physical changes that control pore-scale shale-gas properties. *Extended Abstracts of the Unconventional Resources Technology Conference: Austin, Texas, USA* **2017**, p 7. DOI: 10.15530/urtec-2017-2708858
27. Jew, A. D.; Dustin, M. K.; Harrison, A. L.; Joe-Wong, C. M.; Thomas, D. L.; Maher, K.; Brown, G. E. Jr.; Bargar, J. R., Impact of organics and carbonates on the oxidation and precipitation of iron during hydraulic fracturing of shale. *Energy & Fuels* **2017**, 31 (4), 3643-3658. DOI: 10.1021/acs.energyfuels.6b03220
28. Harrison, A.; Jew, A.; Dustin, M.; Thomas, D.; Joe-Wong, C.; Bargar, J. R.; Johnson, N.; Brown, G. E. Jr.; Maher, K., Element release and reaction-induced porosity alteration during shale-hydraulic fracturing fluid interactions. *Applied Geochemistry* **2017**, 82. DOI: 10.1016/j.apgeochem.2017.05.001
29. Kiss, A.; Jew, A.; Joe-Wong, C.; Maher, K.; Liu, Y.; Brown, G.; Bargar, J., Synchrotron-based transmission x-ray microscopy for improved extraction in shale during hydraulic fracturing. *SPIE: Optical Engineering + Applications*, **2015**; Vol. 9592. DOI: doi:10.1117/12.2190806

# Publications / Presentations

## Invited Presentations at National Meetings and Departmental Seminars

30. Jew, A.D. Geochemical alterations in unconventional oil/gas shales: Impact of base fluids and additives, Texas Water & Environmental Institute, University of Texas-Permian Basin, June 25, 2021 [Invited].
31. Gundogar, A.S.; Ross, C.M.; Li, Q.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale imaging of core flooding experiments during transport of reactive fluids in fractured unconventional shales, 2020 SPE Western Regional Meeting, Bakersfield, CA (Manuscript submitted on March 5, 2020) [Invited].
32. Jew, A.D. (2020) Field laboratories: a data driven approach for basin specific research. Presented at the Unconventional Resources Technology Conference. Austin, TX. Jul 20-22. [Invited]
33. Druhan, J. L.; Ling, B.; Davila, G.; Battiato, I. (2019) Imaging the reactive transport properties of sedimentary formations across scales. Presented at the AGU Fall Meeting. Dec 9-13, San Francisco, CA. [Invited]
34. Noël, V.; Fan, W.; Druhan, J.; Jew, A. D.; Li, Q.; Kovscek, A.; Brown, G. E. Jr.; Bargar, J. R. (2019) X-ray imaging of tracer reactive transport in unconventional shales. Presented at the CMC-UF all hands meeting, Stanford University. Oct 24. Palo Alto, CA. [Invited]
35. Jew, A. D.; Li, Q.; Cercone, D.; Brown, G. E. Jr.; Bargar, J. R. (2019) A New approach to controlling barium scaling in unconventional systems. Presented at the Unconventional Resources Technology Conference (URTeC). Apr. 22. Pittsburgh, PA. [Invited]
36. Bargar, J. R.; Jew, A. D.; Harrison, A. L.; Kiss, A.; Kohli, A.; Li, Q.; Maher, K.; Brown, G. E. Jr. (2017) Geochemistry of shale-fluid reactions at pore and fracture scales. Presented at the Goldschmidt Geochemistry conference. Aug 16. [Invited]

# Presentations

37. Bargar, J. R.; Kiss, A.; Kohli, A.; Harrison, A. L.; Jew, A. D.; Dustin, M.; Joe-Wong, C.; Maher, K.; Brown, G. E. Jr.; Zoback, M.; Liu, Y.; Cercone, D. (2016) Geochemistry of shale-fluid reactions at pore and fracture scales. Presented at the 252nd American Chemical Society National Meeting. Aug 21. [Invited]
38. Bargar, J. R.; Brown, G. E. Jr.; Dustin, M. K.; Harrison, A. L.; Jew, A. D.; Joe-Wong, C.M.; Maher, K. (2015) Geochemical control of shale fracture and matrix permeability. Presented at the Shales without Scales Workshop. Santa Fe, USA. June 10. [Invited]
39. Bargar, J. R.; Brown, G. E. Jr.; Dustin, M. K.; Harrison, A. L.; Jew, A. D.; Joe-Wong, C.M.; Maher, K. (2015) Geochemical control of shale fracture and matrix permeability. Presented at Baker Hughes Incorporated, Tomball, USA, July 14. [Invited]

**Talks and Posters Presented at National Meetings.**

40. Gundogar, A.S.; Druhan, J.L., Ross, C.M.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Core-flood Effluent and Shale Surface Chemistries in Predicting Interaction between Shale, Brine, and Reactive Fluid. Accepted by **2021** URTeC Annual Conference. [Oral]
41. Jew, A.D.; Bargar, J.R.; Brownlow, J.W.; Laughland, M. Rethinking Mineral Scaling: What, Where, and Why is it occurring in the stimulated rock volume. Accepted by **2021** URTeC Annual Conference. [Oral]
42. Spielman-Sun, E.; Jew, A.D.; Druhan, J.L.; Bargar, J.R. Controlling Strontium Scaling in the Permian Basin through Manipulation of Base Fluid Chemistry and Additives. Accepted by **2021** URTeC Annual Conference. [Oral]
43. Ding, J.; Clark, A.C.; Vanorio, T.; Jew, A.J.; Bargar, J.R. Quantifying shale fracture properties from elastic stress sensitivity. Accepted by **2021** URTeC Annual Conference. [Oral]

# Presentations

44. Gundogar, A.S.; Ross, C.M.; Li, Qingyun; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale Imaging of Core Flooding Experiments during Transport of Reactive Fluids in Fractured Unconventional Shales. Presented at *SPE Western Regional Meeting*, 20 April 2021 [Presented as Invited Speaker].
45. Gundogar, A.S.; Kovscek, A.R. Predicting Interactions Between Shale, Brine, and Fracture Fluid Using Reactive Core-Floods. Presented at 2021 *SUPRI-A Annual Affiliates Meeting*, 21-22 April 2021 [Oral Presentation].
46. Spielman-Sun, E.; Jew, A.D.; Bargar, J.R. The impact of acid-base stimulation sequence on mineral stability for tight/impermeable unconventional rocks: Delaware Basin case study. American Institute of Chemical Engineers (AIChE) Annual Meeting. Virtual. Nov 16-20, 2020
47. Gundogar, A.S.; Ross, C.M.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale Investigation of Reactive Fluid Transport Characteristics in Unconventional Shales. Presented at AGU 2020 Fall Meeting [Virtual poster].
48. Jew, Adam D.; Spielman-Sun, Eleanor; Li, Qingyun; Ding, Jihui; Gundogar, Asli; Vanorio, Tiziana; Clark, Anthony; Brown, Gordon E., Jr.; Bargar, John R. Impact of Geochemistry on Unconventional Shale Efficiency and Mineral Scale Production: Clay-rich versus Carbonate-rich Shales. Clay Mineral Society Pacific Northwest National Laboratory Richland, WA October 18-23, 2020.
49. Bargar, John R., Basin-specific geochemistry to promote unconventional efficiency. DOE-FE Office of Oil and Natural Gas Fundamental Research Project Review Virtual Meeting, Pittsburgh, PA, Oct 16, 2020. [Oral]
50. Spielman-Sun, Eleanor; Jew, Adam D.; Bargar, John R. (2020) The impact of acid-base stimulation sequence on mineral stability for tight/impermeable unconventional rocks: Delaware Basin case study. Presented at the Stanford Synchrotron Radiation Lightsource (SSRL) Users' Meeting. Sept. 28-Oct. 9, 2020. [Poster]

# Presentations

51. Jew, Adam D.; Bargar, John R.; Brownlow, Josh; Laughland, Matt (2020) The Importance of Base Fluids for Water Management in Unconventional Reservoirs. Presented at the Stanford Synchrotron Radiation Lightsource (SSRL) Users' Meeting. Sept. 28-Oct. 9, 2020. [Poster]
52. Ding, J.; Clark, A. C.; Vanorio, T.; Jew, A. D.; Bargar, J. R. (2020) Time-lapse acoustic monitoring of fracture alteration in Marcellus shale. Presented at the Unconventional Resources Technology Conference. Austin, TX. Jul 19-22. [Oral]
53. Jew, A.D.; Bargar, J.R.; Brownlow, J.; Laughland, M. (2020) Strontium behavior in Midland Basin unconventional reservoirs: the importance of base fluids. Presented at the Unconventional Resources Technology Conference. Austin, TX. Jul 19-22. [Oral]
54. Bargar, John R., Basin-specific geochemistry to promote unconventional efficiency. DOE-FE Office of Oil and Natural Gas Fundamental Shale Research Program Virtual Briefing, July 14, 2020. [Oral]
55. Gundogar, A.S.; Ross, C.M.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. (2020) Multiscale Imaging of Reactive Fluid Transport in Fractured Shales. Presented at the SUPRI-A Annual Affiliates Meeting. Stanford, CA. June 11 [Oral].
56. Gundogar, A.S.; Ross, C.M.; Li, Q.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. (2019) Multiscale imaging characterization of fracture fluid migration and reactive transport in shales. Presented at the AGU Fall Meeting. San Francisco, CA. Dec 9-13. [Poster]
57. Noël, V.; Fan, W.; Bargar, J.R.; Druhan, J.; Jew, A.D.; Li, Q.; Brown, G.E. Jr. (2019) Synchrotron x-ray imaging of reactive transport in unconventional shales. Presented at AGU Fall Meeting, symposium H44B: porous media across scales: from interfacial properties to subsurface processes. San Francisco, CA. Dec 12. [Oral]

# Presentations

SLAC

58. Li, Q.; Jew, A. D.; Brown G. E. Jr.; Bargar, J. R.; Maher, K. (2019) Reactive transport in shale matrix after fracturing fluid imbibition. Presented at the American Institute of Chemical Engineers (AIChE) Annual Meeting, Orlando, FL. November 10-15. [Oral]
59. Noël, V.; Fan, W.; Bargar, J.R.; Druhan, J.; Jew, A.D.; Li, Q.; Kovscek, A.R; Brown, G. E. Jr. (2019) Synchrotron x-ray imaging of reactive transport in unconventional shales. Presented at the SSRL annual users meeting, Menlo Park, CA. Sept 25. [Poster]
60. Jew, A. D.; Harrison, A.; Li, Q.; Cercone, D. P.; Maher, K.; Bargar, J. R.; Brown, G. E. Jr. (2019) Unconventional mineralogy: interactions of hydraulic fracturing fluids with minerals and organic matter in unconventional and tight oil formations. Presented at the Geological Society of America Annual Meeting. Phoenix, AZ. September 23. [Talk]
61. Li, Q.; Jew, A. D.; Bargar, J. R.; Lopano, C. L.; Hakala, A. J.; Stuckman, M. Y. (2019) Shale-gas-fluid interaction for water and energy. Presented at the ACS National Meeting & Exposition. Orlando, FL. March 31. [Talk]
62. Jew, A. (2018) Pore Scale Control of Gas and Fluid Transport at Shale Matrix-Fracture Interfaces. Presented research at Mastering the subsurface through technology innovation partnerships and collaboration: carbon storage and oil and natural gas technologies review meeting, Pittsburgh, PA, Aug. 13-16, 2018. [Talk]
63. Hakala, A.; Morris, J.; Bargar, J. R.; Birkholzer, J. (2018) Fundamental shale interactions-DOE National Laboratory Research. Presented at the DOE Upstream Workshop. Houston, TX. Feb. 14. [Talk]
64. Jew, A. D.; Cercone, D.; Li, Q.; Dustin, M. K.; Harrison, A. L.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown, G. E. Jr.; Bargar, J. R. (2017) Chemical controls on secondary mineral precipitation of Fe and Ba in hydraulic fracturing systems. Presented at the American Institute of Chemical Engineers (AIChE) Annual Meeting, Minneapolis, MN. Oct. 29-Nov. 3. [Talk]

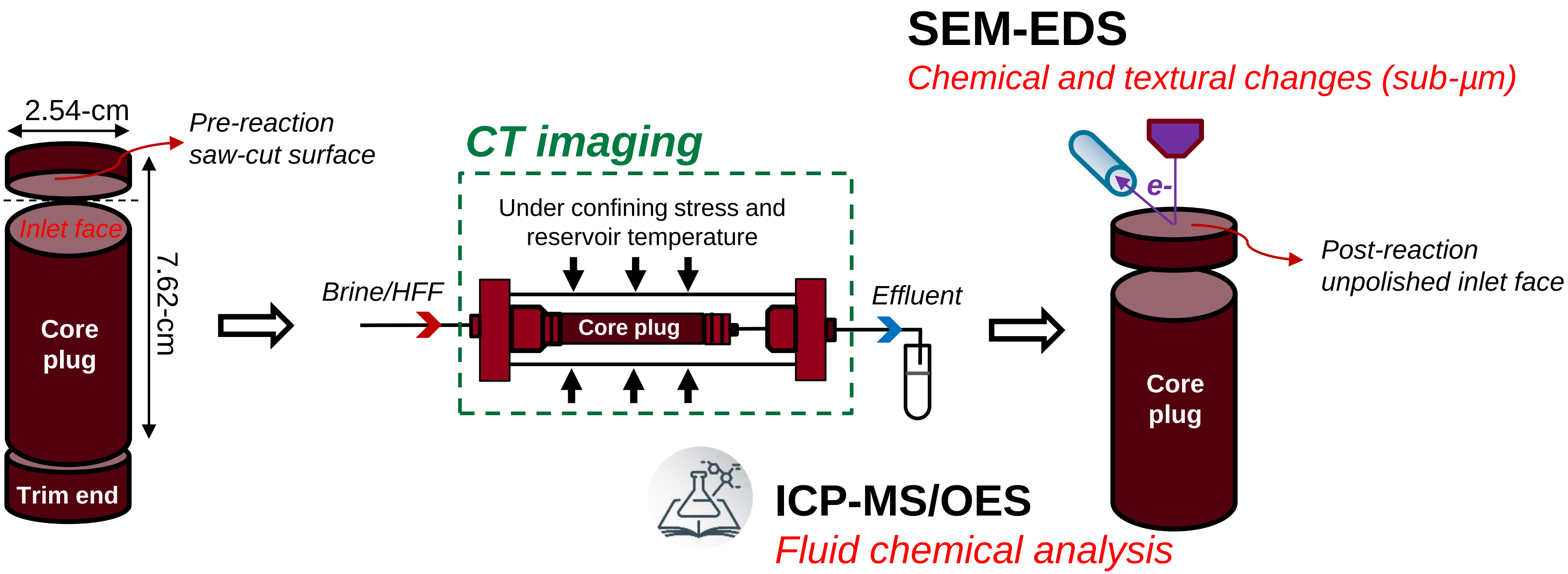
# Presentations

65. Li, Q.; Jew, A. D.; Brown, G. E. Jr.; Bargar, J. R. (2017) Chemical reactivity of shale matrixes and the effects of barite scale formation. Presented at the AGU Fall Meeting. New Orleans, LA. Dec. 11-15. [Talk]
66. Jew, A. D.; Dustin, M. K.; Harrison, A. L.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown G. E. Jr.; Bargar J. R. (2016) The Importance of pH, oxygen, and bitumen on the oxidation and precipitation of Fe(III)-(oxy)hydroxides during hydraulic fracturing of oil/gas shales. Presented at the American Geophysical Union Fall Meeting. San Francisco, USA. December 13. [Talk]
67. Bargar, J. R.; Kiss, A.; Kohli, A.; Harrison, A. L.; Jew, A. D.; Lim, J.-H.; Liu, Y.; Maher, K.; Zoback, M.; Brown, G. E. Jr. (2016) Synchrotron X-ray imaging to understand porosity development in shales during exposure to hydraulic fracturing fluid. Presented at the American Geophysical Union Fall Meeting. San Francisco, USA. December 12. [Talk]
68. Harrison, A. L.; Maher, K.; Jew, A. D.; Dustin, M. K.; Kiss, A.; Kohli, A.; Thomas, D. L.; Joe-Wong, C.; Brown G. E. Jr.; Bargar, J. R. (2016) The Impact of Mineralogy on the Geochemical Alteration of Shales During Hydraulic Fracturing Operations. Presented at the American Geophysical Union Fall Meeting. San Francisco, USA. December 13. [Talk]
69. Harrison, A.; Maher, K.; Jew, A.; Dustin, M.; Kiss, A.; Kohli, A.; Thomas, D.; Joe-Wong, C.; Liu, Y.; Lim, J.-H.; Brown, G. E. Jr.; Bargar, J. (2016) Physical and chemical alteration of shales during hydraulic fracturing. Presented at the Goldschmidt Conference, Yokohama, Japan. June 29. [Talk]
70. Dustin, M. K.; Jew, A. D.; Harrison, A. L.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown G. E. Jr.; Bargar, J. R. (2015) Kerogen-hydraulic fracture fluid interactions: reactivity and contaminant release. Presented at the American Geophysical Union Fall Meeting. San Francisco, USA. December 14-18. [Talk]
71. Harrison, A. L.; Jew, A. D.; Dustin, M. K.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown, G. E. Jr.; Bargar, J. R. (2015) A geochemical framework for evaluating shale-hydraulic fracture fluid interactions. Presented at the American Geophysical Union Fall Meeting. San Francisco, USA. December 14-18. [Talk]

# Presentations

72. Jew, A. D.; Joe-Wong, C.; Harrison, A. L.; Thomas, D. L.; Dustin, M. K.; Brown, G. E. Jr.; Maher, K Bargar, J. R. (2015) Iron release and precipitation in hydraulic fracturing systems. Presented at the American Geophysical Union Fall Meeting. San Francisco, USA. December 14-18. [Talk]
73. Joe-Wong, C.; Harrison, A. L.; Thomas, D. L.; Dustin, M. K.; Jew, A. D.; Brown, G. E. Jr.; Maher, K.; Bargar, J. R. (2015) Coupled mineral dissolution and precipitation reactions in shale-hydraulic fracturing fluid systems. Presented at the American Geophysical Union Fall Meeting. San Francisco, USA. December 14-18. [Talk]
74. Harrison, A. L.; Jew, A. D.; Dustin, M. K.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown, G. E. Jr.; Bargar, J. R. (2015) A geochemical framework for evaluating shale-hydraulic fracture fluid interactions. Presented at the Stanford Center for Secure Carbon Storage Research Seminar. Stanford, USA. October 21. [Talk]
75. Dustin, M. K.; Jew, A. D.; Harrison, A. L.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown, G. E. Jr.; Bargar, J. R. (2015) Kerogen-hydraulic fracture fluid interactions: reactivity and contaminant release. Presented at the Stanford Synchrotron Radiation Lightsource user's meeting. Stanford, USA. Oct 7-9. [Talk]
76. Harrison, A. L.; Jew, A. D.; Dustin, M. K.; Joe-Wong, C.; Thomas, D. L.; Maher, K.; Brown G. E. Jr.; Bargar, J. R. (2015) A geochemical framework for evaluating shale-hydraulic fracture fluid interactions. Presented at the Stanford Synchrotron Radiation Lightsource User's Meeting, Stanford, USA, Oct 7-9. [Talk]

# Main tool: Time-lapse X-ray CT to monitor coreflood progress and data for model calibration




- **Sequencing of injectants: Vacuum evacuate → Kr Inj (for porosity)→ Re-Vacuum → Brine Inj → HFF Inj (at 80°C) → Kr inj (for porosity)**
- Elemental analysis of effluent species (ICP-MS/OES) and SEM-EDS surface analysis
- Elements measured: *Na, Mg, Al, Si, P, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Mo, Ba*

# Results: Multiscale effects