#### SILIC NATIONAL ACCELERATOR LABORATORY



U.S. DEPARTMENT OF

OFFICE OF OIL & NATURAL GAS

Fossil Enerav



# Basin-specific geochemistry to promote unconventional efficiency

FUNDAMENTAL RESEARCH PROJECT REVIEW MEETING

October 16, 2020

### **Address barriers to production: geochemistry**

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

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

1 mm Barte in microcracks and in matrix

3. *Very* low intrinsic permeability

### Important knowledge gaps

What geochemical parameters control mineral scale - in different basins?

Can we monitor mineral scale and fractures simultaneously?



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



Team



geochemistry



transport

physics

modeling

Experimental geochemistry

geochemistry

### **Understand and Mitigate Mineral Scale**



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

cm's



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

cm's



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





Fe<sup>2+</sup>

Fe<sup>3+</sup>

20 µm



### Marcellus



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

cm's

#### Wolfcamp





### **Characterization & Simulation**



#### Sulfate scaling is basin specific



Barite is universal problem; Degree of problem is basin specific

#### What factors control barite scale in shale?

 How to compare wells w/different in fluids, shale mineralogy, well bore conditions?

- Distance-based Generalized Sensitivity Analysis (DGSA) was adapted to our reactive transport model on shale-HFF interactions
- Controlling factors for barite formation were obtained:



Less important factors (ranked):

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- Fluid mass
- Pyrite abundance
- Diffusion coefficient
- Sulfate concentration
- Iron scale in fluid

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Li et al. (2020) in review

Sulfate generation > Initial barite abundance > barite saturation/rates > salinity/pH/temp ~ porosity

#### Is iron mineral scale equally problematic in all reservoirs? Bone Spring, Delaware (Permian) Basin





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Aqueous chemistry

As carbonate concentration increases, fluid pH increases, and Fe(II)  $\rightarrow$  Fe(III) oxidation rate increases

Fe(III) scale accumulates in matrix next to Fe(II) source

77

Less clogging of matrix and fractures



## **Rock Physics for Monitoring Flow Pathways**



# **Velocity Signatures of Flow Pathways**

Soft, clay-rich formation after acidizing: velocity cannot discriminate producing (propped) fractures from non-producing ones!



Stiff, clay-rich formation: producing (propped) fractures can be seismically detected!

### **Manipulate porosity**



Can we manipulate porosity to improve flow through fracture faces?

Gundogar



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Industry & research community

#### **Establishment of an altered zone**

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



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

*The solution*: Manipulate chemistry and injection pressure to promote an altered zone.



Average CT-number profiles (CT-number proportional to bulk shale density)



#### **Establishment of an altered zone**

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

*The solution*: Manipulate chemistry and injection pressure to promote an altered zone.



**Average CT-number profiles** (CT-number proportional to bulk shale density) 2700 2680 ~3 cm **L** 2660 2640 2620  $\backslash M$ HFF Average 2600 2580 Vacuum BEFORE 2560 Vacuum AFTER 2540 1 2 3 5 6 7 8 Core length (cm)

 SEM reveals dissolution features of calcite cleavage planes





### Use models to mitigate scale



#### How do we fix scale production: Case study of Celestite

#### Base fluid water types:

- Freshwater: low salinity, low SO<sub>4</sub><sup>2-</sup>/Sr<sup>2+</sup>
- Brackish groundwater: high salinity, High SO<sub>4</sub><sup>2-</sup>/low Sr<sup>2+</sup>
- Clean brine (cleaned produced water): highest salinity, low SO<sub>4</sub><sup>2+</sup>/High Sr<sup>2+</sup>

#### Experimental results





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#### Accomplishments:

Accomplishments

- Published 16 manuscripts; 1 in review; 3 in preparation: Fe, Ba, and Sr scale formation mechanisms
- Developed & patented acid-swap mitigation for Ba scale
- Providing water treatment targets for Sr scale mitigation
- Working with 3 industrial partners to use new scale mitigation knowledge in industrial practices
- Discovered/quantified organic-mediated Fe oxidation and scale precipitation mechanisms
- Introduced new technologies for unconventional geochemistry monitoring

# cripts; 1 in review; 3 in 🚃







#### **Synergies & Opportunities**



#### **National Laboratory Partners**



#### **Industrial Partners**











# **THANK YOU!**

# Appendices

#### **Benefit to the Program**

#### **Program goals addressed:**

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

# Fracture-fluid interfaces are crucial





- Modeling is crucial to testing process models and finding weaknesses in understanding of shale geochemistry
- Comparing shale-fluid reactivity across basins, compositions is critical to developing geochemical and geomechanical insights
- Laboratory-based surface imaging techniques (SEM) can not be used to study reactions/precipitation occurring in shale matrix



#### 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 necessary portion 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.

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**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**



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

#### **Gantt Chart: Tasks 1-2**

| Tack     | Title  | 1        | Month of project |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
|----------|--|----------|------------------|-------|-------|-----|-----|-----------|-----|--------|--------|-----|-------|---------|-----|------------|---------|--------|-----|---------|-----|----------|----------|-----|------------|---------|---------|-----------|---------|-----|-------|---------------|--------|--------------------------|-------|--------|--------|-----|---------|
| TOSK     | inte   | 0        |                  |       |       |     |     |           |     |        |        |     |       | CY 2021 |     |            |         |        |     |         |     |          |          |     |            | CY 2022 |         |           |         |     |       |               |        |                          |       |        |        |     |         |
|          |  | FY 2019  |                  |       |       |     |     |           |     |        | FY 202 | 0   |       | 010     |     |            | FY 2021 |        |     |         |     |          |          |     |            |         | EY 2022 |           |         |     |       |               |        |                          |       |        |        |     |         |
|          |  | 1        | 2 3              | 1 4   | 5     | 6   | 7   | 8         | 9   | 10 11  | 12     | 13  | 14 1  | 5 16    | 17  | 18 1       | 19 2    | 0 21   | 22  | 23 24   | 25  | 26       | 27 28    | 29  | 30         | 31 32   | 33      | 34        | 35 36   | 37  | 38    | 39 /          | 40 41  | 42                       | 43    | 44 4   | 5 46   | 47  | 48      |
|          |  | Oct      | Nov De           | ec Ja | 1 Feb | Mar | Apr | May       | Jun | Jul Au | z Sep  | Oct | Nov D | ec Jan  | Feb | Mar A      | pr M    | av Jun | Jul | Aug Sep | Oct | Nov      | Dec Jan  | Feb | Mar        | Apr Ma  | / Jun   | Jul       | Aug Sep | Oct | Nov D | Dec J         | an Feb | Mar                      | Apr N | lav Ju | in Jul | Aug | Sep     |
| 1        | Task 1. Project management   |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 1.1      | Development/Refinement of PMP  |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 1.2      | Quarterly research performance reports                                 |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       | 1             |        |                          |       |        |        |     |         |
| 1.3      | Meetings with NETL research groups                                     |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        | 1   |         |
| 1.4      | Annual research performance report                                     |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 1.5      | Final technical report   |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        | 1   |         |
| 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                               |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.1.2  | Complete initial scoping experiments                                   |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.1.3  | React shale with fracture fluid  |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        | 1   |         |
| 2.1.1.4  | Characterize post-reaction shale samples: laboratory-based methods     |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.1.5  | Analyze solution data from reactor experiments                         |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.1.6  | Characterize precipitates: sychrotron-based methods                    |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.1.7  | Initial manuscript draft for subtask 2.1.1                             |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.1.8  | Submit manuscript for subtask 2.1.1                                    |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.2    | Modeling subtask   |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.2.1  | Develop model framework  |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.2.2  | Test reaction networks against new experimental from 2.1.1             |          |                  |       |       |     |     |           |     |        |        |     |       |         | 1   |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.1.2.3  | Model narameter sensitivity analysis for major shale system types      |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         | 1       |           |         |     | -     |               |        |                          | -     |        |        | +   |         |
| 2124     | Reactive transport modeling of systems in 2,1,1                        |          |                  |       |       |     |     |           | -   |        | -      |     |       |         |     |            |         |        |     |         |     |          | -        |     |            | -       |         |           |         |     | -     | -+            |        |                          | -     |        |        | + + |         |
| 2125     | Initial manuscript draft for subtack 2.1.2                             |          |                  | -     |       | +   |     |           | -   | -      | +      |     |       | -       |     |            |         |        |     |         |     |          |          |     |            |         | +       |           |         |     |       |               |        |                          | -     | -      | -      | ++  | _       |
| 212.5    |  |          |                  | _     | _     | -   | -   |           | -   |        | -      | -   |       | -       | -   |            | -       | -      | _   |         |     |          |          |     |            |         |         |           |         |     | -     | -+            | -      |                          |       | -      | -      | ++  |         |
| 2.1.2.0  | Submit manuscript for subtask 2.1.2                                    |          | _                | _     | _     | _   | -   |           | _   |        | -      | -   | _     |         | -   |            | _       | _      |     |         |     |          | _        | -   |            |         |         |           |         |     | _     | _             |        |                          | _     | _      | _      | ++  |         |
| 2.2      | wittigation of mineral scaling in unconventional reservoirs            |          |                  |       | -     | -   | -   |           | _   | _      | -      |     |       | -       |     |            |         | _      | _   |         |     |          |          | _   |            |         | +       |           |         |     | _     | _             |        |                          | _     |        | -      |     | _       |
| 2.2.1    | wodeling task  |          |                  | _     | _     | -   | -   |           |     | _      | -      |     |       | _       | -   |            | -       | _      | -   |         |     |          |          |     |            |         |         |           |         |     |       |               | _      |                          |       | -      | _      | ++  |         |
| 2.2.1.1  | Conduct numerical optimization experiments for each shale system       |          |                  | _     | _     | -   | -   |           |     | _      | -      |     |       | _       | -   |            | -       | _      | -   |         |     |          | _        |     |            |         |         |           |         |     |       |               | _      |                          |       | -      | _      | ++  |         |
| 2.2.1.2  | Evaluate cost/availability of constituents of optimized parameters     |          |                  | _     | _     | -   | -   |           |     | _      | -      |     |       | _       | -   |            | -       | _      | -   |         |     |          | _        |     |            |         | +       |           |         |     |       |               | _      |                          |       | -      | _      | ++  |         |
| 2.2.1.3  | Develop experimental program based on optimizations                    |          |                  | _     | _     | -   | -   |           |     | _      | -      |     |       | _       | -   |            | -       | _      | -   |         |     |          |          |     |            |         |         |           |         |     |       |               | _      |                          |       | -      | _      | ++  |         |
| 2.2.1.4  | Initial manuscript draft for subtasks 2.2.1.1-3                        |          |                  | _     | _     | -   | -   |           |     |        | -      |     |       | _       | -   |            |         | _      |     |         |     |          |          | _   |            |         |         |           |         |     |       | _             | _      |                          |       |        | _      | ++  |         |
| 2.2.1.5  | Submit manuscript for subtasks 2.2.1.1-3                               |          |                  | _     | _     | _   | _   |           |     |        | _      |     |       |         | _   |            |         |        |     |         |     |          |          | _   |            |         | -       |           |         |     |       | _             |        |                          |       |        |        | +   |         |
| 2.2.1.6  | Re-evaluate/refine model as experimental data become available         |          |                  |       | _     |     |     |           |     |        | _      |     |       | _       |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     | _     | _             | _      |                          |       |        |        |     |         |
| 2.2.1.7  | Refine model-based experimental optimization procedure                 |          |                  |       |       |     |     |           |     |        | _      |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.1.8  | Initial manuscript draft for subtasks 2.2.1.6-7                        |          |                  |       |       |     |     |           |     |        | _      |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.1.9  | Submit manuscript for subtasks 2.2.1.6-7                               |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2    | Experimental task  |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.1  | Formulation of new fracture fluid recipes                              |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.2  | Testing of new formulations for various scaling conditions w/out shale |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.3  | React shale with optimized fracture fluid                              |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.4  | Characterize post-reaction shale samples: laboratory-based methods     |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        | 1   |         |
|          | (optimized fluids)   |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        | 1   |         |
| 2.2.2.5  | Analyze solution data from reactor experiments (optimized fluids)      |          | 1                |       |       | 1   |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.6  | Characterize precipitates: sychrotron-based methods (optimized         |          |                  |       |       | 1   |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.7  | Initial manuscript draft for subtask 2.2.1                             |          |                  |       |       | 1   |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.8  | Submit manuscript for subtask 2.2.1                                    |          |                  |       |       | 1   | 1   |           |     |        |        |     |       |         | 1   |            |         |        |     |         |     |          |          | 1   |            |         | 1       |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.9  | Optimize/reformulate fluids  |          |                  |       |       |     |     |           |     |        | 1      |     |       |         | 1   |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.2.2.10 | Be-test new formulations (after reformulating)                         |          |                  |       |       |     |     |           |     |        | 1      |     |       |         | 1   |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     | in Yr 5 |
| 2.2.2.11 | Initial manuscript draft for Tasks 2 2 1 9-10                          |          |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         | 1       |           |         |     |       |               |        |                          | -     |        |        | +   | in Yr 5 |
| 22212    | Submit manuscript for Tasks 2 2 1 9-10                                 |          |                  |       |       |     |     |           | -   |        | -      |     |       | -       | 1   |            |         |        | -   |         |     |          | -        |     |            | -       |         |           |         |     |       |               |        |                          |       |        |        | + + | in Vr 5 |
| 2 3      | Acoustic Measurements on Laboratory reacted shales                     |          |                  | -     | -     | -   |     |           | -   | _      | +      |     |       |         |     |            | -       | _      |     |         |     |          |          |     |            |         | +       |           |         |     | _     | _             |        |                          |       |        | -      | ++  |         |
| 2.3      | SEM images of top and bottom of upreacted shale                        |          |                  |       |       |     |     |           |     |        |        |     |       |         | 1   |            |         |        |     |         |     |          | -        |     |            |         |         |           |         |     |       | -             |        |                          | -     |        |        | +   |         |
| 2.3.1    | Measurement of grain density, bulk density, and peracity (are          |          |                  |       |       |     |     |           |     |        |        |     |       | -       | -   |            | -       | -      | _   |         |     |          | -        | -   |            | -       | -       |           |         |     | _     | -+            | -      |                          |       | -      | -      | ++  |         |
| 2.3.2    | Poset Shale camples with fracture finite                               | +        | <u> </u>         | _     | -     |     |     |           |     |        |        |     |       |         | 1   | <b>⊢</b> + |         | +      |     |         |     | $\vdash$ |          | +   | <u>   </u> |         | 1       |           |         |     |       | +             |        | +                        | +     |        | _      | +   |         |
| 2.3.3    | React share samples with fracture fluid                                | $\vdash$ |                  | _     | _     | +   | +   | $\mapsto$ | -   |        |        |     |       |         |     |            | _       | +      |     |         |     | $\vdash$ | <u> </u> | +   | ++         |         | +       |           |         |     |       | $\rightarrow$ |        | $\mapsto$                | +     | _      | _      | +   |         |
| 2.3.4    | SERVITTAGES OF LOP and DOTTOM OF reacted shale                         | $\vdash$ |                  | _     | _     | +   | -   | $\vdash$  |     |        |        |     |       |         |     |            |         |        |     |         |     | $\vdash$ |          | +   | $\vdash$   |         | 1       | -         | _       |     |       |               | _      | $\vdash$                 | _     |        | _      | +   | _       |
| 2.3.5    | Measurement of grain density, bulk density, and porosity (post-        |          |                  |       |       | 1   |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          | 1   | 1          |         | 1       |           |         |     |       |               |        |                          |       |        |        |     |         |
| L        | reaction)  |          |                  |       | _     | _   | _   | $\square$ |     |        |        |     |       | _       |     |            |         |        |     |         |     |          |          | 1   |            |         | 1       | $\square$ | _       |     |       | $\rightarrow$ |        | $ \downarrow \downarrow$ |       |        |        | +   | _       |
| 2.3.6    | Rock physics modeling  |          |                  |       |       | 1   |     |           |     |        |        |     |       |         | 1   |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.3.7    | Post-injection stress-strain-strength curve measurement                |          |                  |       |       | 1   |     |           |     |        |        |     |       |         | 1   |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.3.8    | Initial manuscript draft for subtask 2.3                               |          |                  |       |       | 1   |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
| 2.3.9    | Submit manuscript for subtask 2.3                                      |          |                  |       |       |     |     |           |     |        |        |     |       |         | 1   |            |         |        |     |         |     |          |          | 1   |            |         | 1       |           |         |     |       |               |        |                          |       |        |        |     |         |
|          |  | LT       |                  |       |       |     |     |           |     |        |        |     |       |         |     |            |         |        |     |         |     |          |          |     |            |         |         |           |         |     |       |               |        |                          |       |        |        |     |         |
|          |  | 1 T      | 1                |       | 1 -   | 1 - | 1   | I T       |     |        |        |     |       | 1 -     | 1 - | 1 1        |         |        | 1 T |         |     | I T      |          | 1   | 1 T        |         | 1       | 1 T       |         |     |       | 1             |        | I T                      |       |        |        | 1   |         |

#### **Gantt Chart: Task 3**

#### Month of project CY 2018 CY 2019 CY 2020 CY 2021 CY 2022 FY 2020 Oct Nov Dec Jan Feb Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep 3 Manipulation of matrix accessibility 3.1 Manipulate rates of dissolution and preciptation 3.1.1 Evaluate literature/ experimental design: stim conditions, parameters 3.1.2 Research/develop stimulation fluid recipes: Marcellus, Midland 3.1.3 Submit synchrotron/neutron user facility proposals 3.1.4 Acquire shale samples 3.1.5 Make up stimulation fluids 3.1.6 Mineral characterization shale samples 3.1.7 Test reactions: Initial scoping experiments 3.1.8 Evaluate/ optimize experiment conditions 3.1.9 Measure permeability of unreacted cores 3.1.10 Collect µ-CT images, unreacted cores 3.1.11 Image processing, unreacted shale cores 3.1.12 Hydrostatic shale core reactions 3.1.13 Collect µ-CT images, unreacted cores 3.1.14 SEM characterization: porosity evolution 3.1.15 XRM maps, unreacted/reacted cores 3.1.16 Measure permeability of reacted cores 3.1.17 Measure porosimetry of unreacted/reacted cores 3.1.18 Initial manuscript draft for subtask 3.1 3.1.19 Submit manuscript for subtask 3.1 3.2 Growth and connectivity of secondary porosity 3.2.1 Test reactions: Initial scoping experiments 3.2.2 Evaluate/ optimize experiment conditions 3.3.3 Pre-characterize samples 3.2.4 React shale samples with fluids 3.2.5 Collect µ/nano-CT images on reacted cores: macroporosity 3.2.6 Image processing, reacted shale cores 3.3.7 2D/SAXS characterization: porosity evolution 3.2.8 SEM (/FIB) characterization: porosity evolution 3.2.9 Initial manuscript draft for subtask 3.2 3.2.10 Submit manuscript for subtask 3.2 3.3 Modeling subtask 3.3.1 Test reaction networks against new experimental from 3.1 3.3.2 Model parameter sensitivity analysis for major shale system types 3.3.3 Reactive transport modeling of systems in 3.1 3.3.4 Initial manuscript draft for subtask 3.2 3.3.5 Submit manuscript for subtask 3.2 3.4 Predict and test optimal conditions 3.4.1 Predict optimal conditions from 3.1, 3.2, 3.3 3.4.2 React shale samples with fluids under optimal conditions 3.4.3 Characterization 3.4.4 Complete initial draft of manuscript for subtask 3.4 in Yr 5 3.4.5 Submit manuscript #3 in Yr 5 No X-rays @ SSRL No X-rays @ SSRL No X-rays @ SSRL No X-rays @ SSRL

#### **Publications**

#### 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. 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 20-22, Austin, TX*, **2020**. DOI: 10.15530/urtec-2020-3016
- 3. 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*. **2020**, 54 (12) 7025-7734. DOI: 10.1021/acs.est.0c01022
- 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**. DOI: 10.1021/acs.energyfuels.9b04542
- 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 Technical Program Expanded Abstracts 2020, pp 2434-2438. DOI: 10.1190/segam2020-3427203.1
- 6. 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**



- 7. 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.
- 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
- 9. 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.
- 10. 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.
- 11. 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.
- 12. 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.
- 13. 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.
- 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

#### **Publications / Presentations**



- 15. 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
- 16. 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
- 17. Kiss, A.; Jew, A.; Joe-Wong, C.; Maher, K.; Liu, Y.; Brown, G.; Bargar, J., Synchrotron-based transmission xray microscopy for improved extraction in shale during hydraulic fracturing. *SPIE: Optical Engineering* + *Applications*, **2015**; Vol. 9592. DOI: doi:10.1117/12.2190806

#### **Invited Presentations at National Meetings and Departmental Seminars**

- 18. 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]
- 19. 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]
- 20. 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]
- 21. 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]
- 22. 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]



- 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]
- 24. 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]
- 25. 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.

- 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 20-22. [Oral]
- 27. 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 20-22. [Oral]
- 28. 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].
- 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]



- 30. 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]
- 31. 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]
- 32. 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]
- 33. 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]
- 34. 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]
- 35. 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]
- 36. 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]
- 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]
- 38. 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]



- 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]
- 41. 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]
- 42. 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]
- 43. 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]
- 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]
- 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]



- 46. 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]
- 47. 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]
- 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]
- 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]