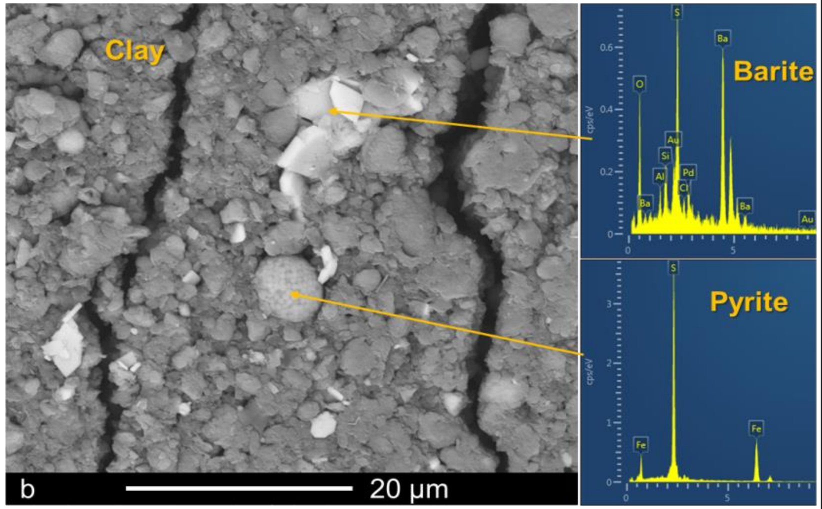
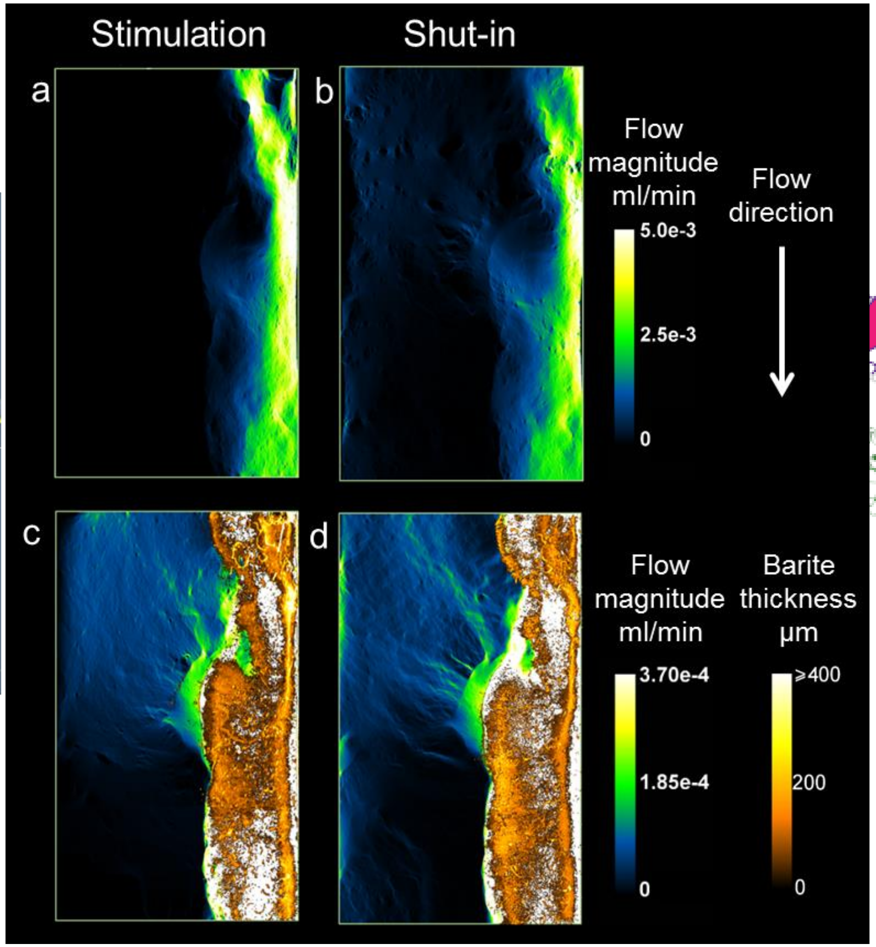
Geochemical Reactions Affecting Reservoir Porosity and Permeability

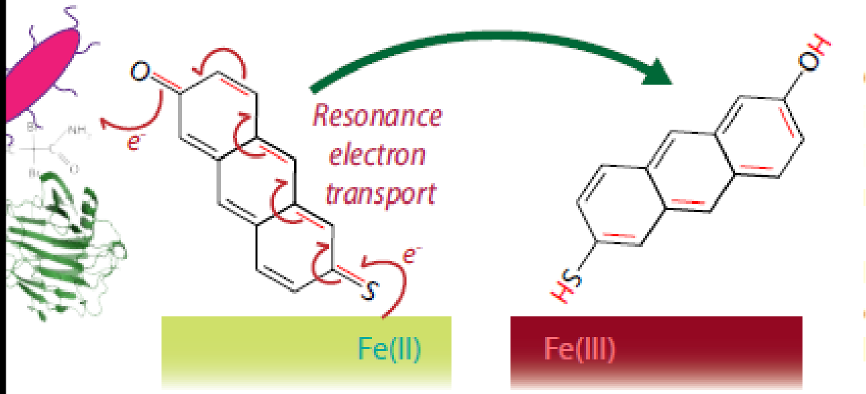
Onshore Unconventional Resources (FWP 1022415 – Task 3)

Alexandra Hakala and Christina Lopano

NETL Research and Innovation Center







FE Oil & Gas Project Review Meeting
October 16, 2020

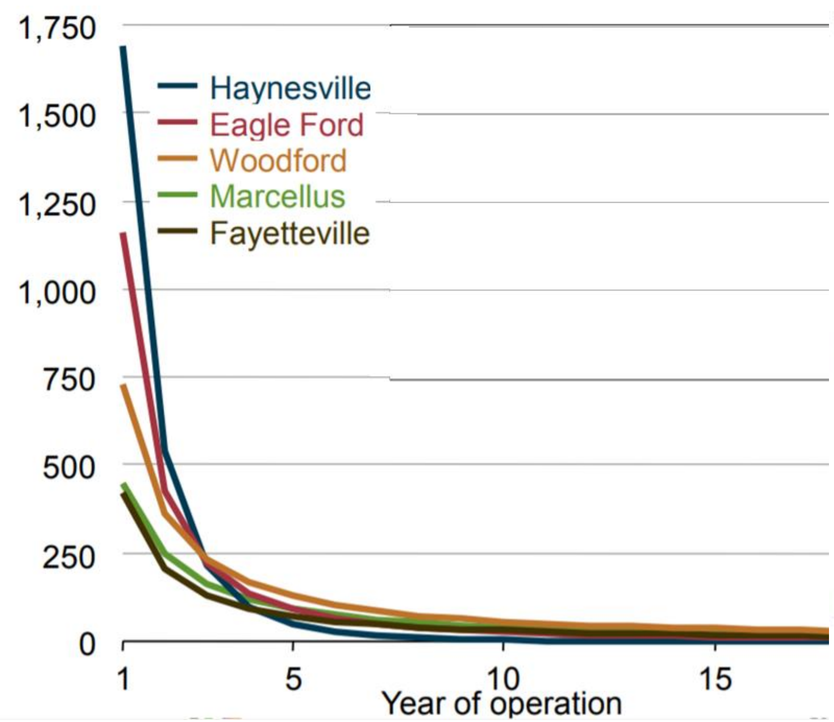
Project team

- Alexandra Hakala, Christina Lopano – PIs
- Wei Xiong – Subtask 3.1 lead
- Brandon McAdams – Subtask 3.2 lead
- Johnathan Moore, Tom Paronish, Karl Jarvis, Bryan Tennant, Mengling Stuckman, Robert Thompson, Rebecca Matecha, Brian Stewart, Rosemary Capo, Shaun Donomyer, Shikha Sharma, Dustin Crandall

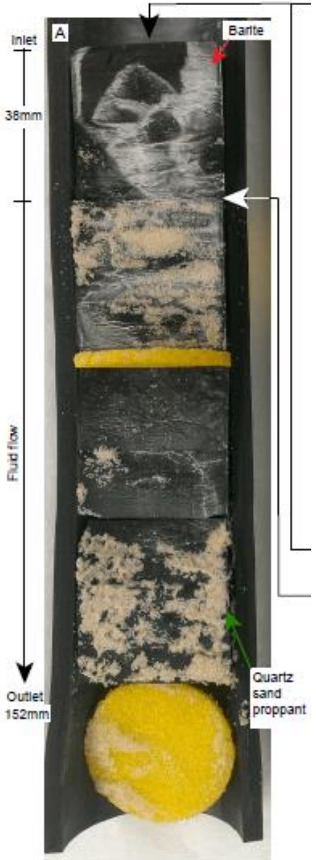
Addressing barriers in unconventional reservoirs – **How chemistry affects flow**

Potential Barriers to Production?

How does chemistry influence production curves? – Permeability alteration



EIA Annual Energy Outlook 2012



Vankeuren et al. ES&T 2017

This project focuses on chemical processes that can impact permeability in hydraulically-generated fractures.

3.1: Geochemical Controls on Mineral Precipitation

- Fluid chemistry and flow pathway impact where fracture face mineral reactions occur
- Chemical reactions change during injection, shut-in, and production
- *Which chemical gradients have the most significant impact?*

3.2: Parameterizing Redox in Hydraulically-Fractured Shales

- Oxidation-reduction reactions influence fracture face mineral reactions
- Limited representation in current models
- *Which parameters need to be quantified in order to best model the system?*

Addressing barriers in unconventional reservoirs – **Technology Benchmarks**

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3.1: Geochemical Controls on Mineral Precipitation

- Fluid chemistry and flow pathway impact where fracture face mineral reactions occur
- Chemical reactions change during injection, shut-in, and production
- *Which chemical gradients have the most significant impact?*

PIOGA Pennsylvania Independent Oil & Gas Association

FUEL

UNCONVENTIONAL RESOURCES TECHNOLOGY CONFERENCE FUELED BY SPE • AAPG • SEG

Ability to predict and model reservoir chemical reactions that impact permeability of significant interest in both conventional and unconventional oil & gas

3.2: Parameterizing Redox in Hydraulically-Fractured Shales

- Oxidation-reduction reactions influence fracture face mineral reactions
- Limited representation in current models
- *Which parameters need to be quantified in order to best model the system?*

JPT JOURNAL OF PETROLEUM TECHNOLOGY

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

Acid-base chemistry is known to impact mineral reactions – little is known about the influence of oxidation-reduction reactions, especially involving organic matter and iron.

Geochemical Reactions Affecting Reservoir Porosity and Permeability – **Major Insights to Date**

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3.1: Geochemical Controls on Mineral Precipitation

- Produced water chemical signals can be used to identify classes of mineral reactions occurring during different operational phases of an unconventional well
- New techniques for characterizing sources of Ba in produced water confirm a significant geologic source, and Ba in shale can promote barite mineral scale nucleation in Marcellus Shale
- High fluid flow across fracture faces relates to increased barite precipitation along primary flow pathways, and different chemical processes control barite precipitation during injection and shut-in operational periods

3.2: Parameterizing Redox in Hydraulically-Fractured Shales

- Oxidation-reduction reactions occur under reservoir conditions, and involve injected fracturing fluid additives + shale minerals

3.1 Geochemical controls on mineral precipitation – Documented chemical changes for different operational periods in hydraulically-fractured reservoir

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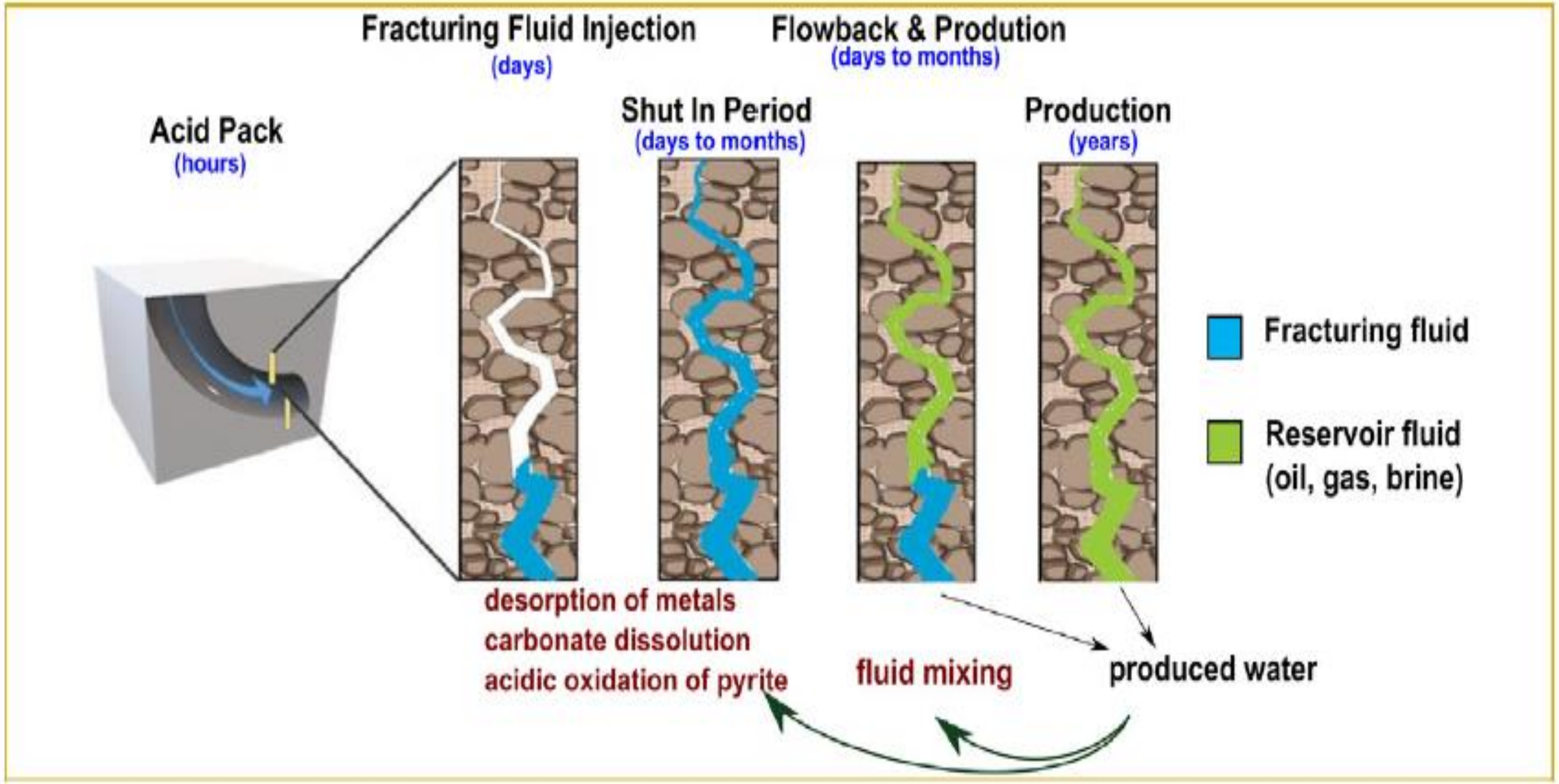
MSEEL Produced Water Reveals Reservoir Chemical Changes

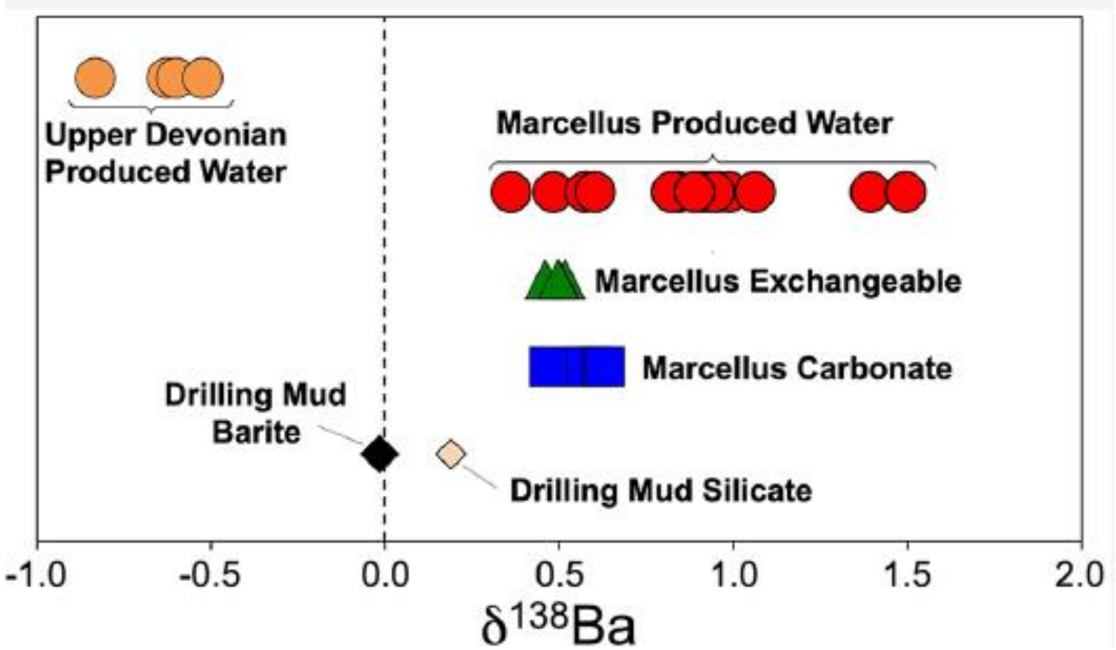


Phan, T.T., Hakala, J.A., Sharma, S. "Application of Geochemical Signals in Unconventional Oil and Gas Reservoir Produced Waters Towards Characterizing In Situ Geochemical Fluid-Shale Reactions." *Science of the Total Environment* (2020).

- **Carbonate dissolution during shut in** – Detected in multiple chemical ratios in early produced water (Sr/Na, Ca/Na, B/Na, and $^{87}Sr/^{86}Sr$)
- **Fracturing chemicals oxidize sulfide minerals** – evidence in trace metal signatures
- **Contact of produced water with clays and organic matter** – ^{6}Li enrichment
- **Fracturing fluid and formation water mixing** – produced water compositional transition
- **Changes in reservoir oxidation state** - Under oxidizing conditions during fracturing period with transition to reducing environment

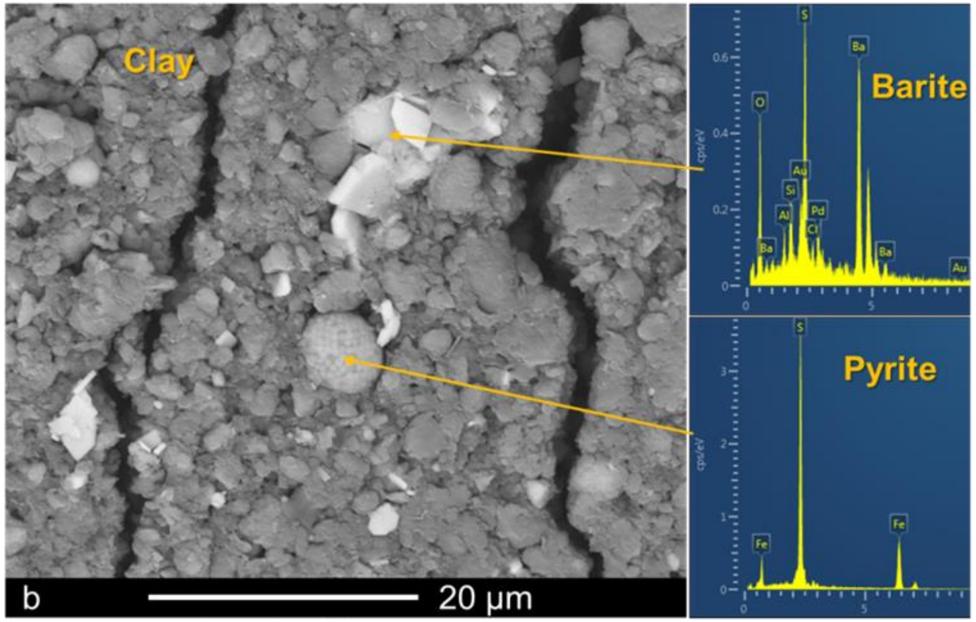
3.1 Geochemical controls on mineral precipitation – Improved techniques for characterizing sources and reactivity of Ba to form barite mineral scale (Marcellus)

Produced water Ba isotope signatures suggest a significant subsurface source



Tieman, Z.G., Stewart, B.W., Capo, R.C., Phan, T.T., Lopano, C.L., Hakala, J.A. "Barium Isotopes Track the Source of Dissolved Solids in Unconventional Shale Gas Produced Water." *Environmental Science and Technology* (2020).

Fluid-mineral reactions can promote reservoir barite precipitation, even with treated water



Wei Xiong, Christina Lopano, Alexandra Hakala, BJ Carney "Investigation of Barite Scaling During Reaction between Pre-Treated Hydraulic Fracturing Fluid from the Field and Marcellus Shale." URTeC Paper 2374, for URTeC 2020 Austin, TX.

3.1 Geochemical controls on mineral precipitation – High flow rate results in greater barite precipitation along the fracture face

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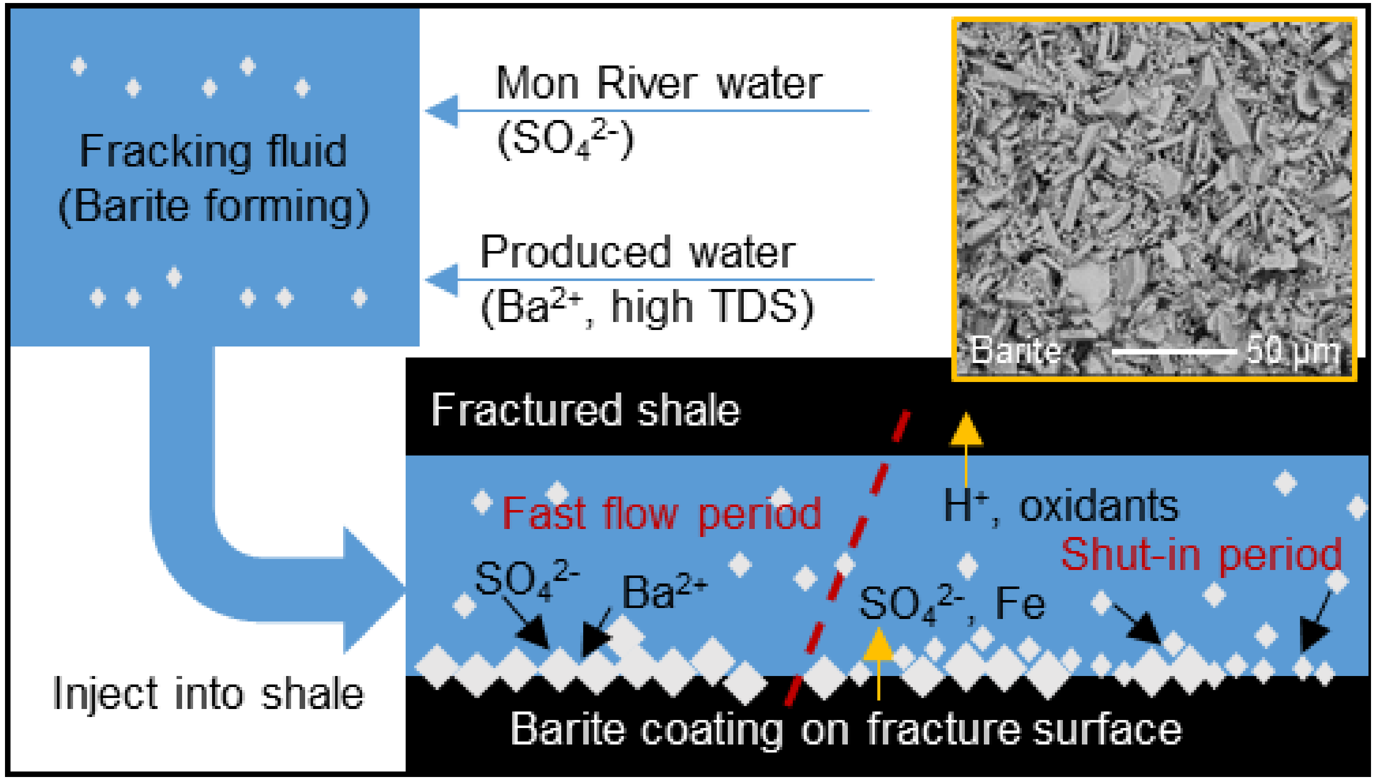
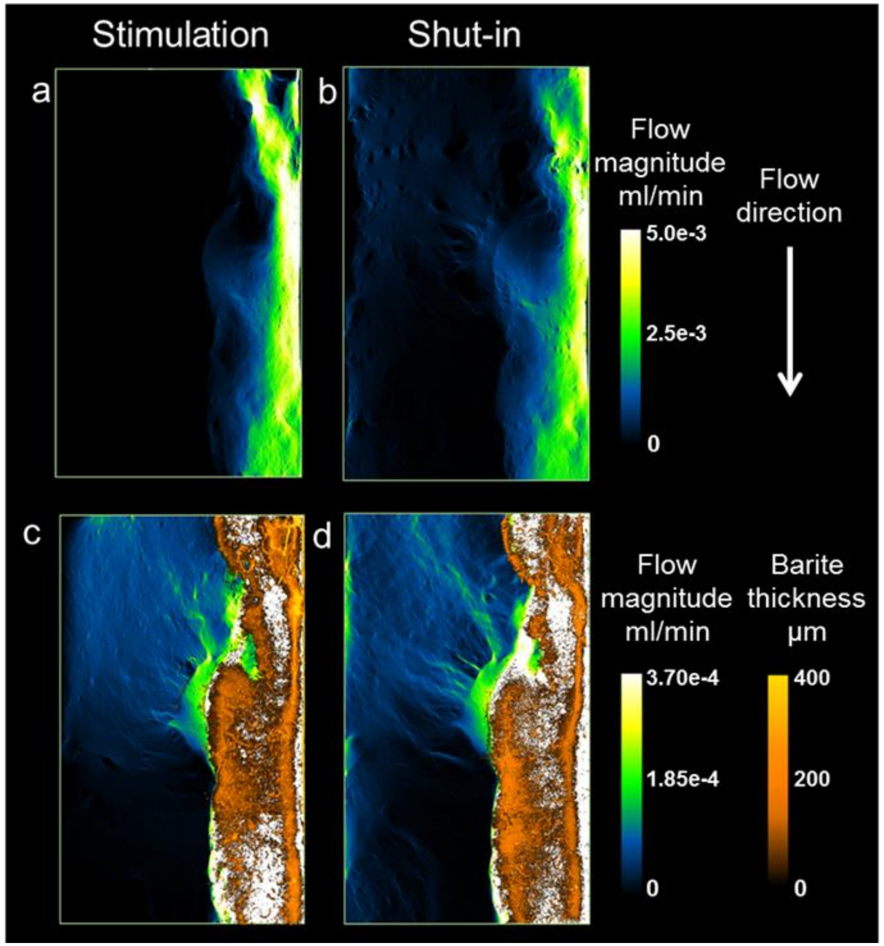
Documented differences in barite scale precipitation under injection vs. shut-in conditions





Wei Xiong, Magdalena Gill, Johnathan Moore, Dustin Crandall, J. Alexandra Hakala, Christina Lopano "Influence of Reactive Flow Conditions on Barite Scaling in Marcellus Shale during Stimulation and Shut-in period of Hydraulic Fracturing," *(Energy & Fuels, 2020)*

3.1 Geochemical Controls on Mineral Precipitation – Effects of fracture face reactions on near-matrix zone

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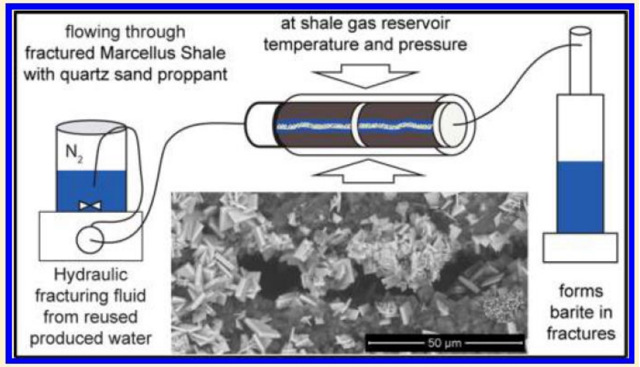
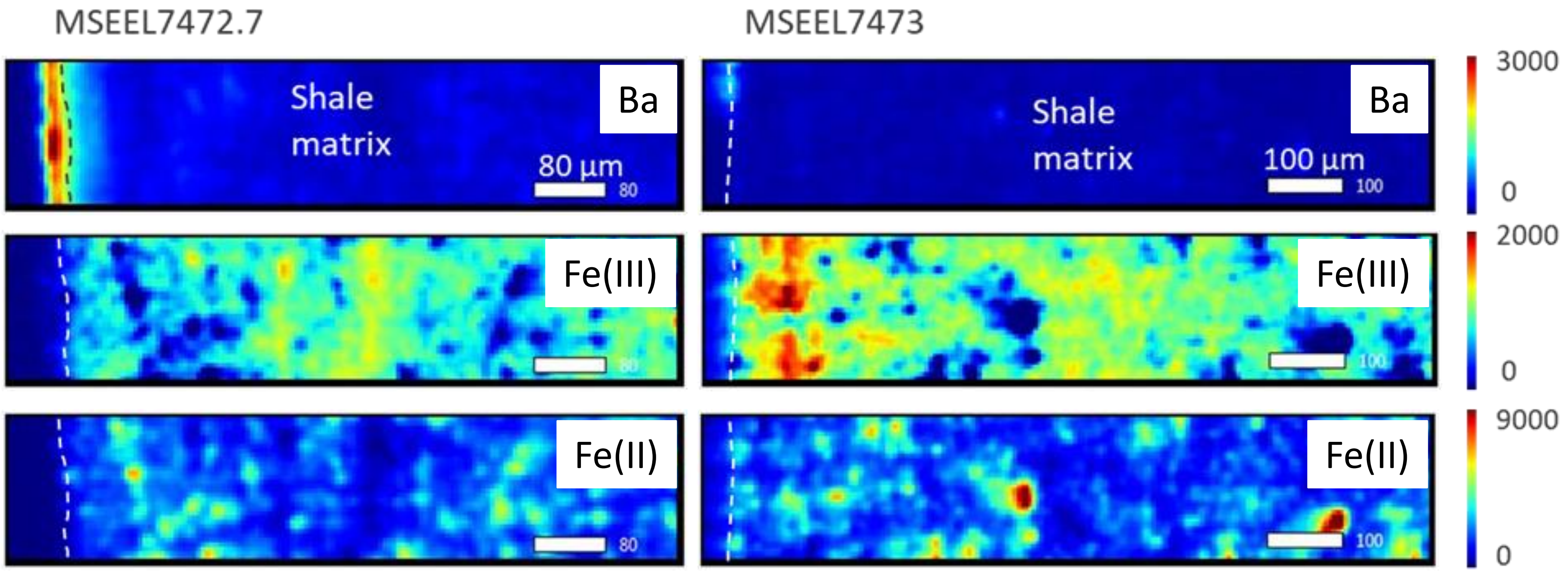
Fracture surface coating is influenced by fluid composition and flow rate, the operational period of a well, and impacts shale matrix reactions



Significant fracture face barite coating | **Limited fracture face barite coating**

Less matrix alteration | **Greater matrix alteration**



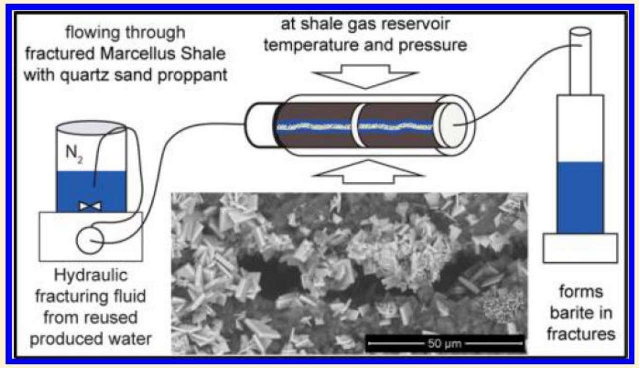
Ba^{2+} + SO_4^{2-} → **Ba**SO_4 (barite)

Fe(II) + oxidant → **Fe(III)** + (other chemical species)

FeS_2 + oxidant → **Fe(II)** + SO_4^{2-} + (other chemical species)

3.1 Geochemical Controls on Mineral Precipitation – Insights and Next Steps

Fracture surface coating is influenced by fluid composition and flow rate, the operational period of a well, and impacts shale matrix reactions



Significant fracture face barite coating | **Limited fracture face barite coating**

Less matrix alteration | **Greater matrix alteration**

Impact on proppant embedment and *fracture* permeability?

Changed *matrix* permeability?

Final Project Period (FY21 funding):

- 3.1: Characterize difference between expected near-wellbore vs. extended fracture network chemical conditions that influence fracture face mineral reactions

Geochemical Reactions Affecting Reservoir Porosity and Permeability – **Major Insights to Date**

NATIONAL ENERGY TECHNOLOGY LABORATORY

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3.2: Parameterizing Redox in Hydraulically-Fractured Shales

- Oxidation-reduction reactions occur under reservoir conditions, and involve injected fracturing fluid additives, shale organic matter, and shale minerals
- Organic matter is a significant mediator in controlling electron transfer between fluids and shale

How do organic and redox geochemistry relate to the mineral scale issues identified by prior experimental efforts?

Acid Pack	Fracturing Fluid Injection	Shut In Period	Flowback & Production	Production
hours	days	days to months	days to months	years

pH 0 — pH 2 — pH 4-6 — pH 6-8

pH neutralizes over time – reaction + fluid mixing

Oxidizing — Reducing

What is reactive during this redox transition?

Majority of Fluid-Shale Reaction Chemistry R&D – Focus on Acid-Base Frac Fluid-Shale Reactions

Limited Data on Redox Reactions – Next Critical Frontier in UOG Geochemistry Research

Changes in electron donating-accepting capacity of fluid & shale components require quantification for effective predictive modeling!

3.2 Parameterizing redox in hydraulically-fractured shales – Surfactants chemically oxidize in the reservoir

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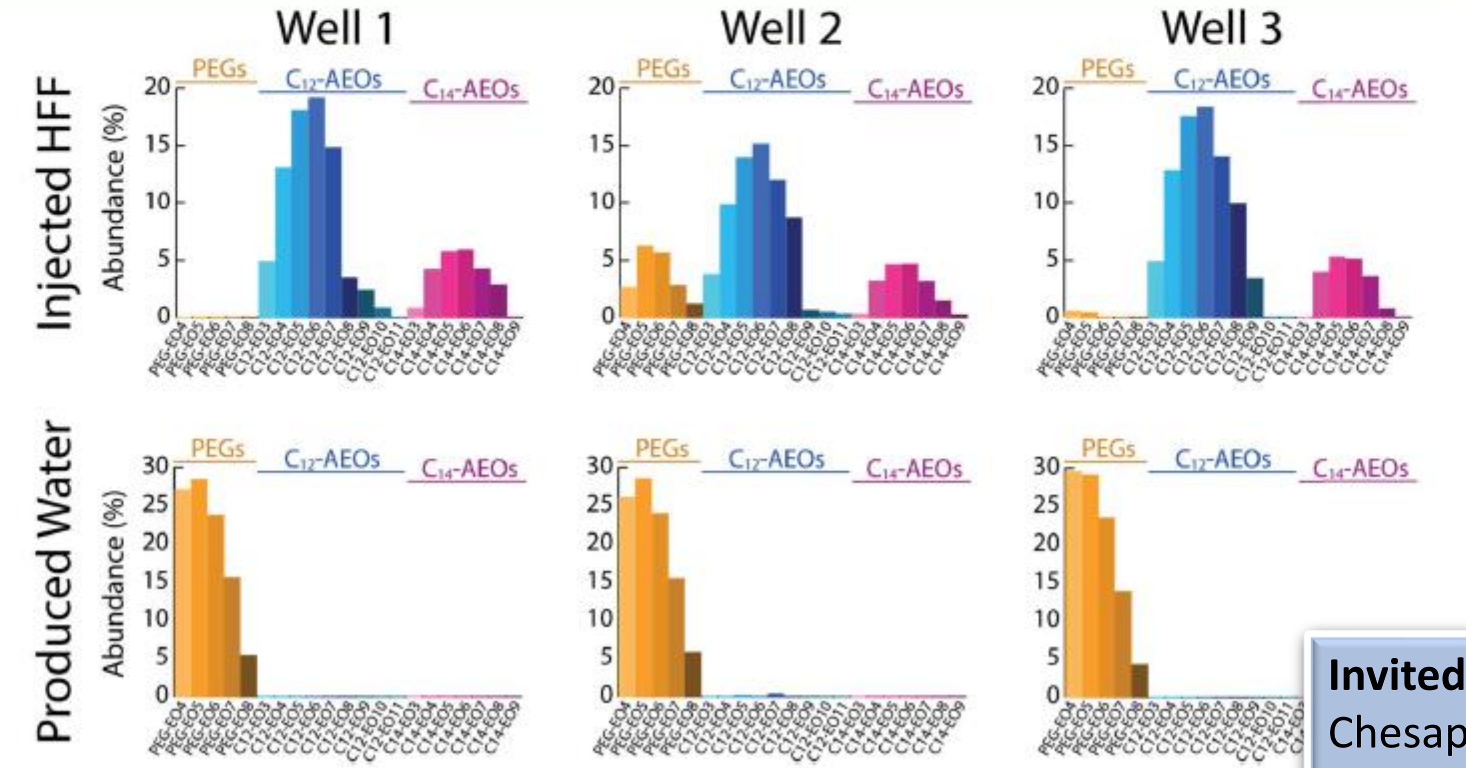
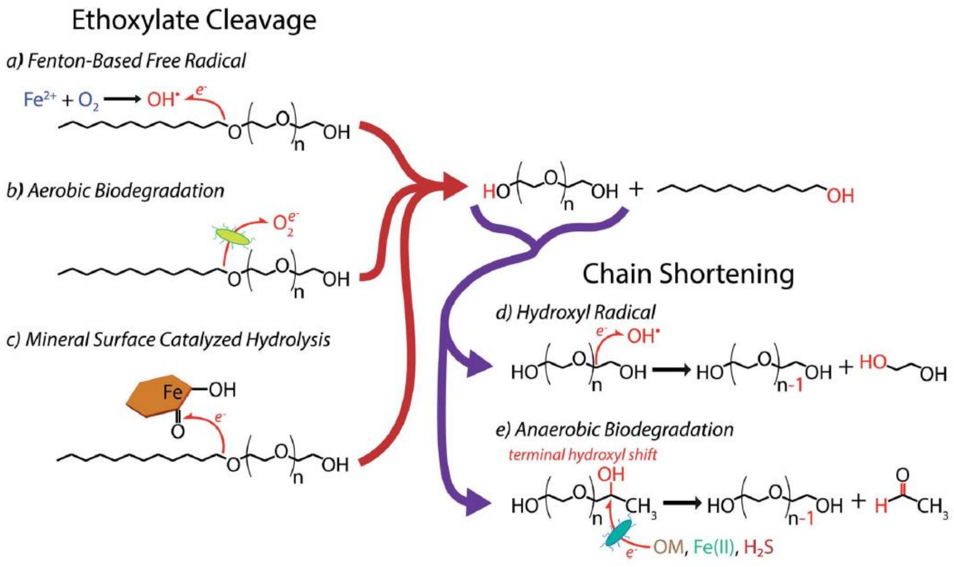
Demonstrated that surfactants chemically change in the reservoir, and likely are impacted by oxidation-reduction reactions (Marcellus Shale)



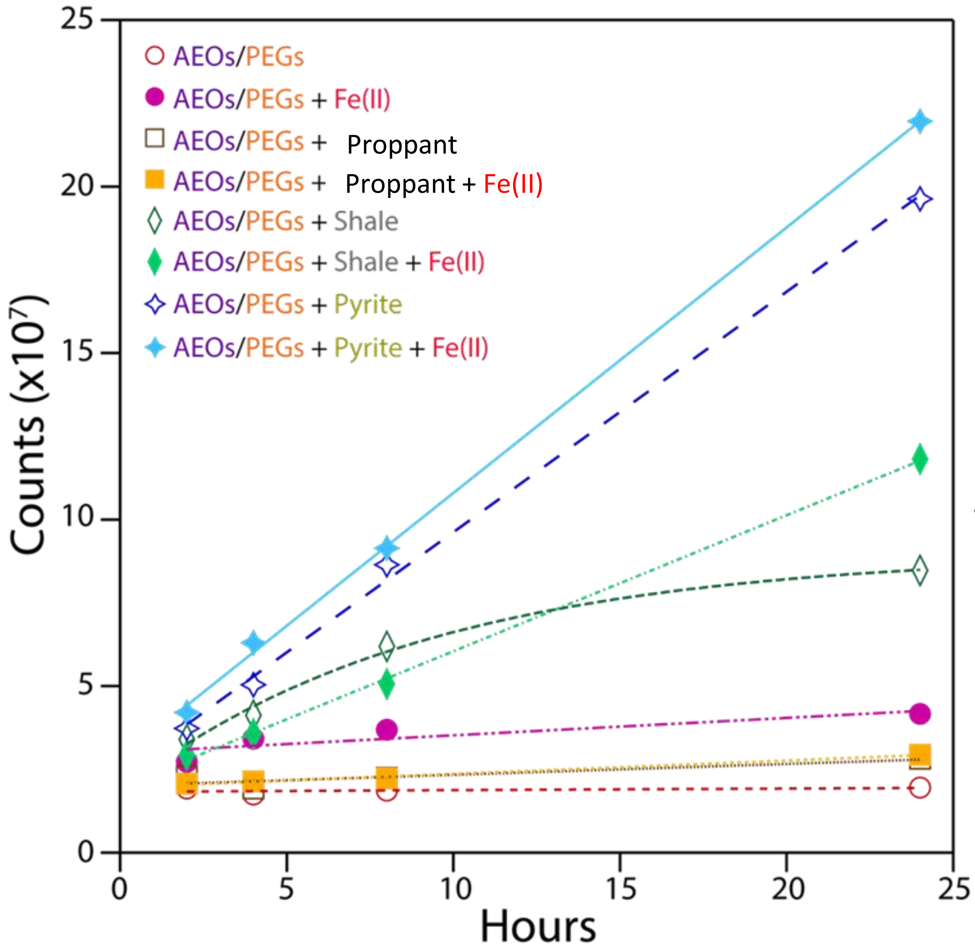


Brandon C. McAdams, Kimberly E. Carter, Jens Blotevogel, Thomas Borch, J. Alexandra Hakala "In situ transformation of hydraulic fracturing surfactants from well injection to produced water." *Environmental Science Processes & Impacts*, 2019.

Invited to present surfactant study and results to Chesapeake Energy – Environmental Defense Fund – RmC3 Consulting Produced Water Toxicity Technical Exchange group (January 30, 2020, web-based meeting)

3.2 Parameterizing redox in hydraulically-fractured shales – Pyrite impacts surfactant reactions

Most significant surfactant transformation occurs when pyrite is present



With Pyrite = Fastest Reactions

With Marcellus Shale (containing pyrite) = Faster than Reaction Without Mineral Fe source

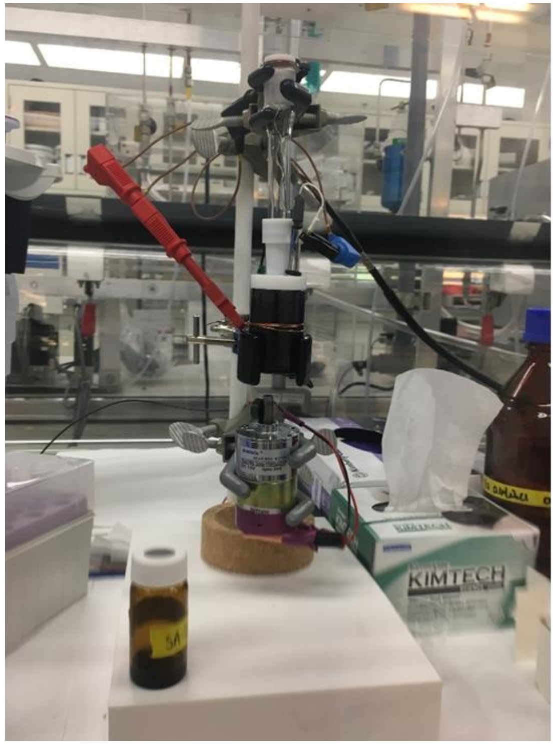
Without Shale or Pyrite = Slowest Reactions

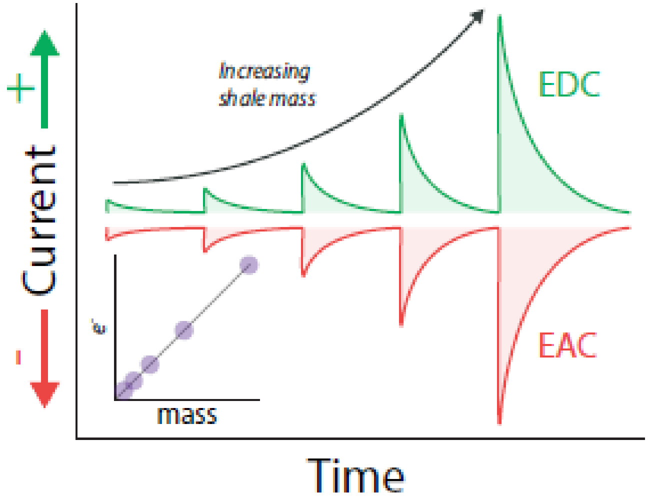
URTeC Presentation on Surfactant-Pyrite Reactions Gained Attention from the Journal of Petroleum Technology – recent article focused on how reactions between injected chemicals, pyrite, and iron in the reservoir can affect production (September 1, 2020)

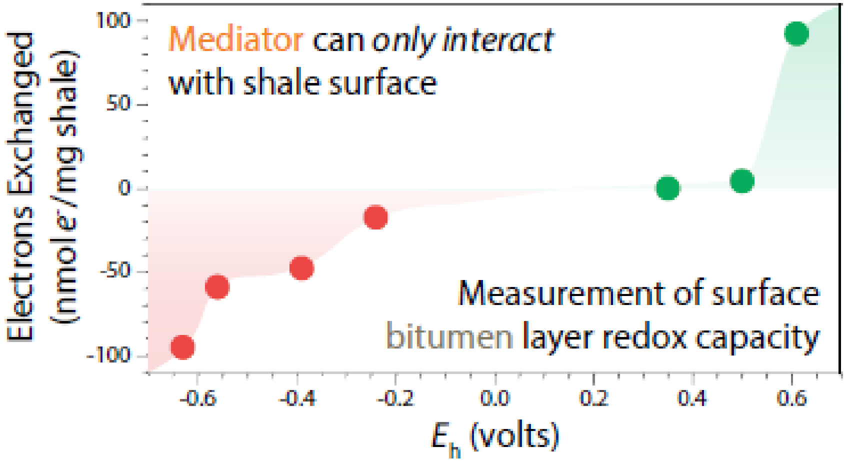
Brandon C. McAdams, Lauren C. Burrows, J. Alexandra Hakala "Abiotic Transformation Kinetics of Surfactants used in Hydraulic Fracturing Fluid." URTeC 2019, Denver, CO.

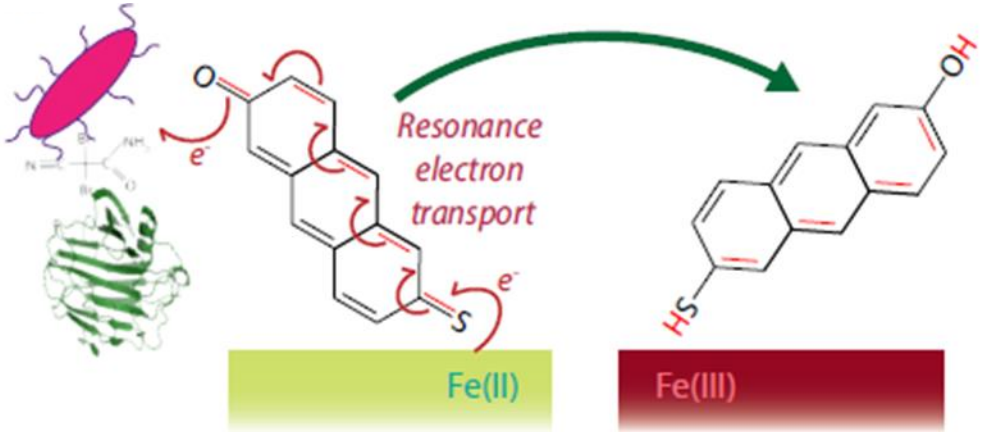
3.2 Parameterizing redox in hydraulically-fractured shales – Identifying shale components that control electron transfer reactions

Organic matter plays a major role in electron transfer between fracturing fluid and shale









Oxidation of electron donating groups in surfacial organic layer may trigger inorganic mineral oxidation through resonance electron transport.

Bitumen may effectively catalyze oxidation of inorganic shale minerals by acting as an electron mediator.

3.2 Parameterizing redox in hydraulically-fractured shales – Electron transfer reactions in the reservoir

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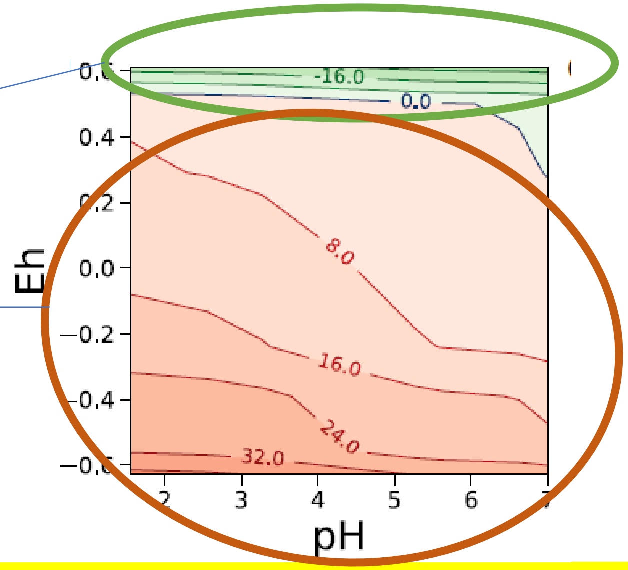
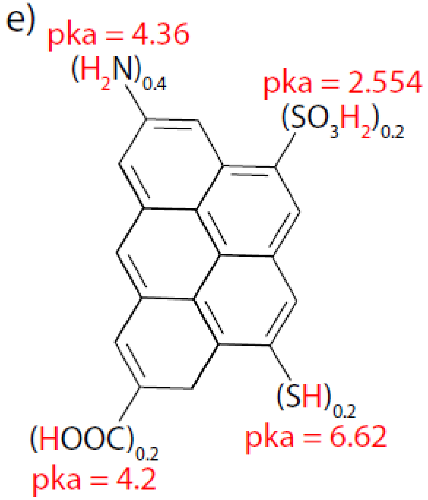
Quantifying electron transfer between fluid and shale will provide redox rate information for reservoir geochemical models

Example for electron transfer plot for a 50% efficiency of reversal electron transfer reaction

e^- transferred from organic matter (shale is oxidized)

e^- transferred to organic matter (shale is reduced)





<u>Final Project Period (FY21 funding):</u>

- 3.2:
  - Evaluate electron donating and accepting capacity for shales with a range of mineral and organic content. (March 2021)
  - Complete development of new inputs to improve the ability for existing models to capture key geochemical reactions in fractured unconventional reservoirs. (March 2022)

Concluding Remarks

Project Insights-to-date, 1 of 2

- Produced water chemical signals can be used to identify classes of mineral reactions occurring during different operational phases of an unconventional well
- New techniques for characterizing sources of Ba in produced water confirm a significant geologic source, and Ba in shale can promote barite mineral scale development in Marcellus Shale
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Concluding Remarks

Project Insights-to-date, 2 of 2

- Oxidation-reduction reactions occur under reservoir conditions, and involve injected fracturing fluid additives, shale organic matter, and shale minerals

- Organic matter is a significant mediator in controlling electron transfer between fluids and shale

Concluding Remarks

Remaining Project Objectives

- **Project End: March 2022**
  - Subtask 3.1
    - Characterize difference between expected near-wellbore vs. extended fracture network chemical conditions that influence fracture face mineral reactions
  - Subtask 3.2:
    - Evaluate electron donating and accepting capacity for shales with a range of mineral and organic content.
    - Complete development of new inputs to improve the ability for existing models to capture key geochemical reactions in fractured unconventional reservoirs.

- **End Product:** Qualitative and quantitative information on which geochemical reactions affect flow pathways, for incorporation into model-based predictions.