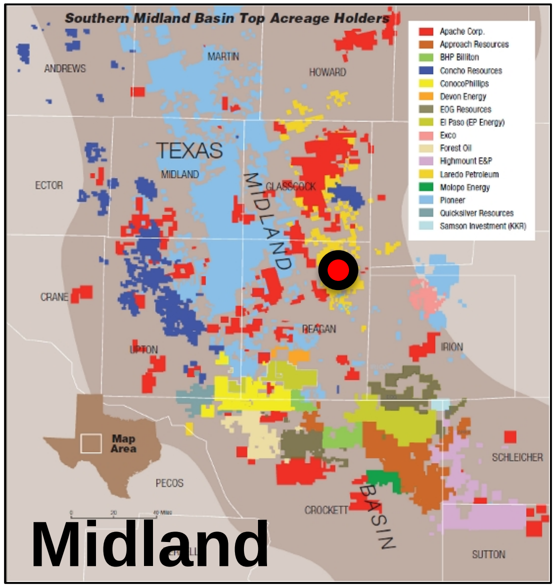
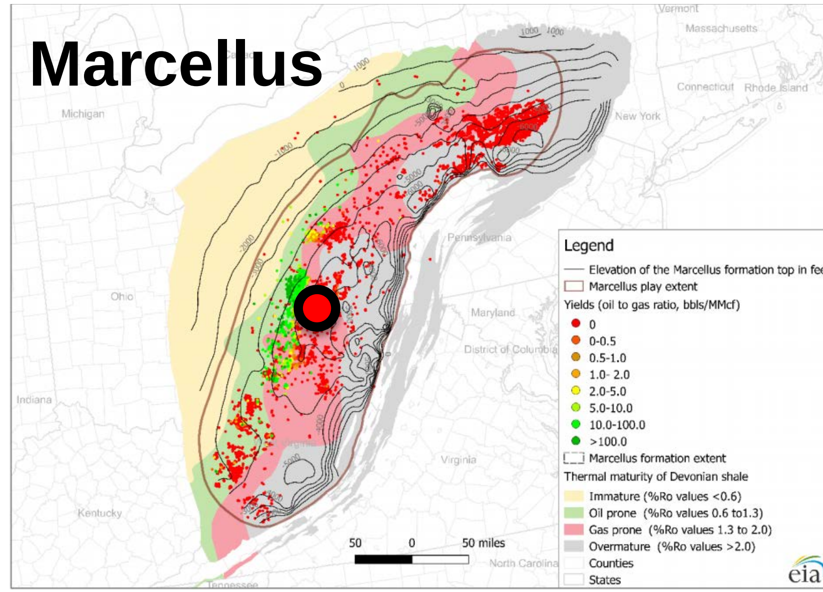
SLAC NATIONAL ACCELERATOR LABORATORY





Basin-specific geochemistry to promote unconventional efficiency

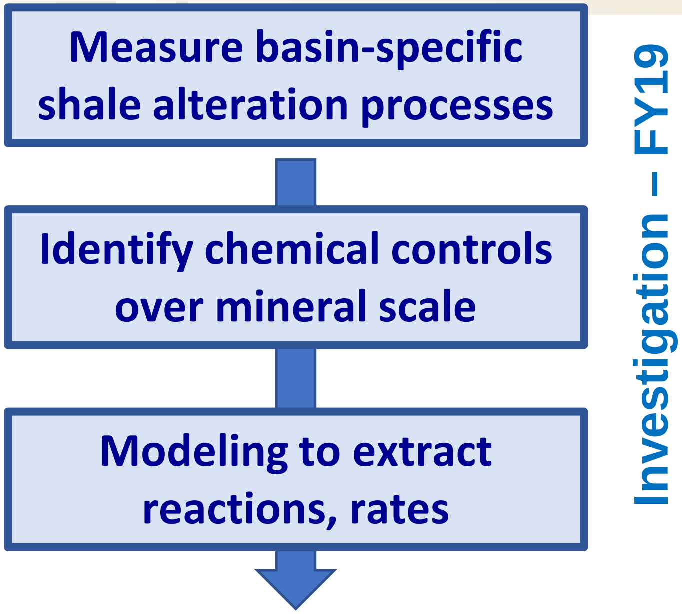
U.S. DEPARTMENT OF ENERGY
Office of Fossil Energy

John Bargar

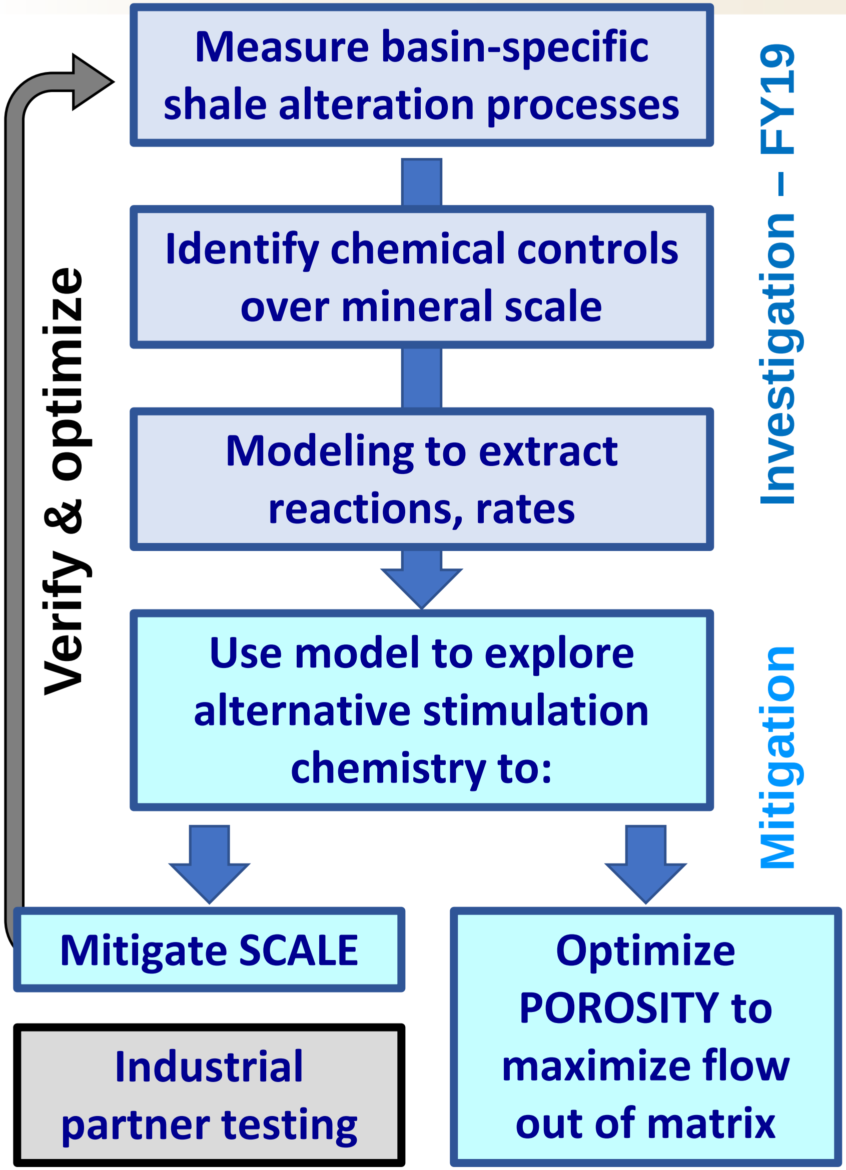
Office of Oil and Natural Gas

Aug 26, 2019

Comprehensive approach to geochemical optimization



Comprehensive approach to geochemical optimization



Comprehensive approach to geochemical optimization

SLAC

Verify & optimize

Measure basin-specific shale alteration processes

Identify chemical controls over mineral scale

Modeling to extract reactions, rates

Investigation – FY19

Use model to explore alternative stimulation chemistry to:

Mitigation

Mitigate SCALE

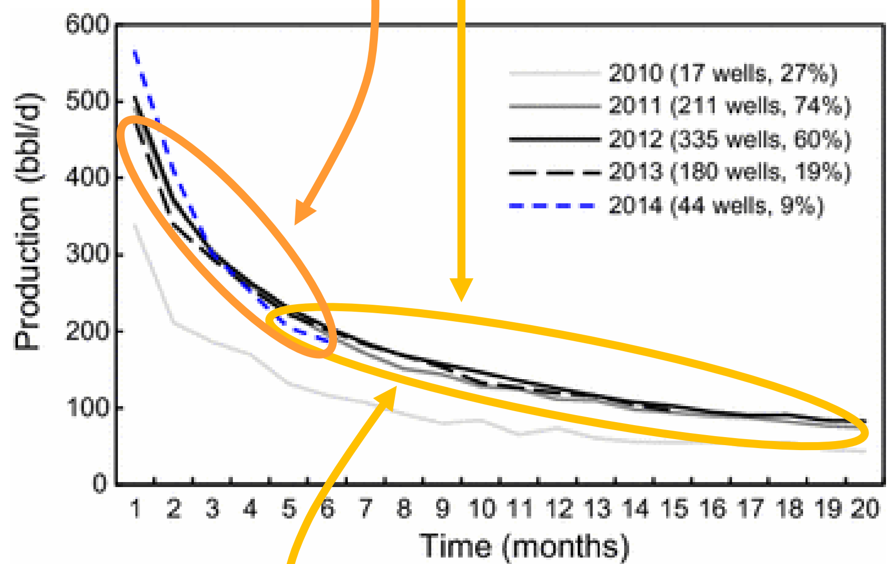
Optimize POROSITY to maximize flow out of matrix

Industrial partner testing

What chemical parameters control scale in different basins?

How can we mitigate unconventional scale?

Can we monitor scale and fractures simultaneously?



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

Can we manipulate reactions to improve flow through altered zone?

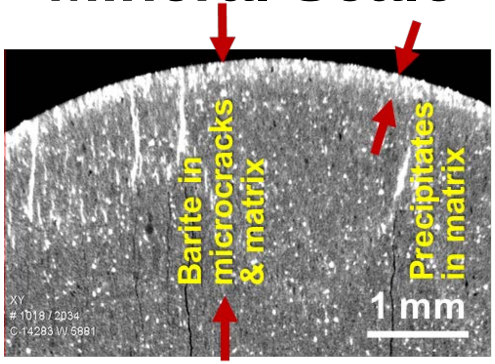
Geochemistry Drivers

Improve efficiency and recovery factors

Improve water reuse

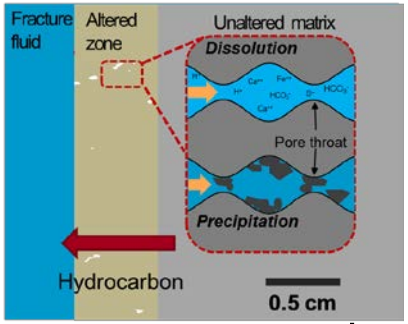
- National energy security
- Environmental footprint
- Water security
- Economics of production

Mineral Scale



Task 2

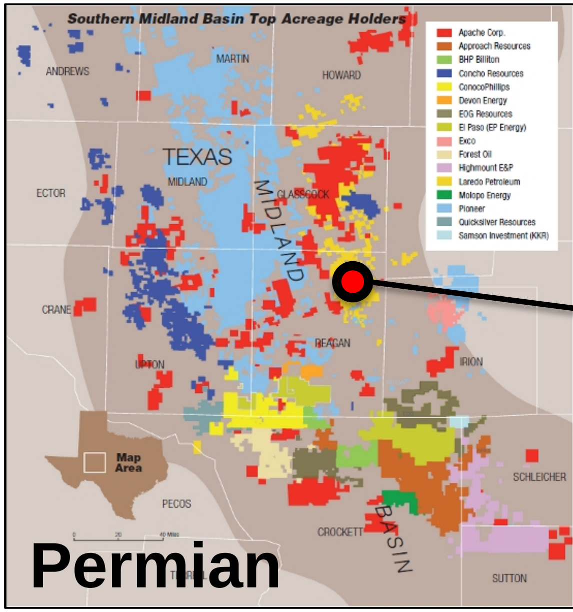
Matrix access



Task 3

> Ryan Flynn, executive director of the New Mexico Oil and Gas Association, a trade group representing up to 900 oil and gas operators in New Mexico, said **water reuse is the industry's "No. 1" priority, as fresh water becomes scarce, and the industry looks to cut back on its environmental impact**.
>
> *Carlsbad Current-Argus, May 19, 2019*

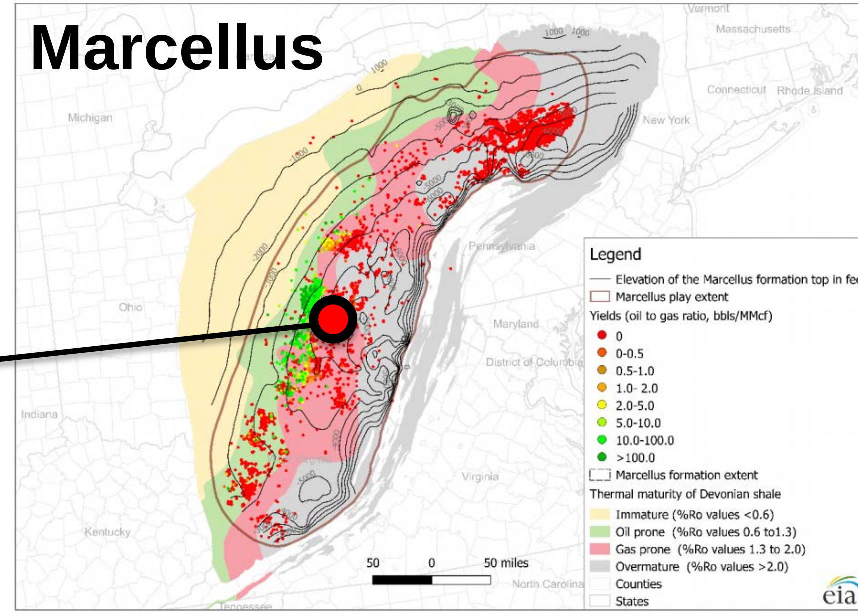
Geochemistry varies across basins



Field labs

HFTS

MSEEL



Oil **Gas**

- Mineralogy, rock microstructure
- Injection sequence, fluid chemistry, water supply (fresh vs reuse)
- Universal problems: Iron scale, low recovery
- Play specific scale problems
  - Strontium- Permian
  - Barium/Radium- Marcellus

Industrial partners

PIONEER NATURAL RESOURCES

Permian / Midland

equinor

Marcellus / Utica

Collaborations, partnerships, and acknowledgements

SLAC

- NETL
- LBNL
- LLNL
- Pioneer Natural Resources
- Equinor

Technical status

Task 2: Scale Geochemistry

2.1 Scale prediction

What chemical parameters control scale in different basins?

2.2 Scale mitigation

Develop chemical strategies to mitigate scale.

2.3 In-situ scale monitoring

Can we monitor scale and fractures simultaneously?

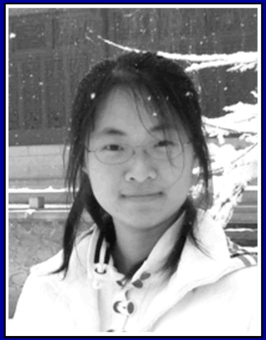
Task 2: Scale Geochemistry

2.1 Scale prediction

What chemical parameters control scale in different basins?

Jew

Li



Spielman-Sun

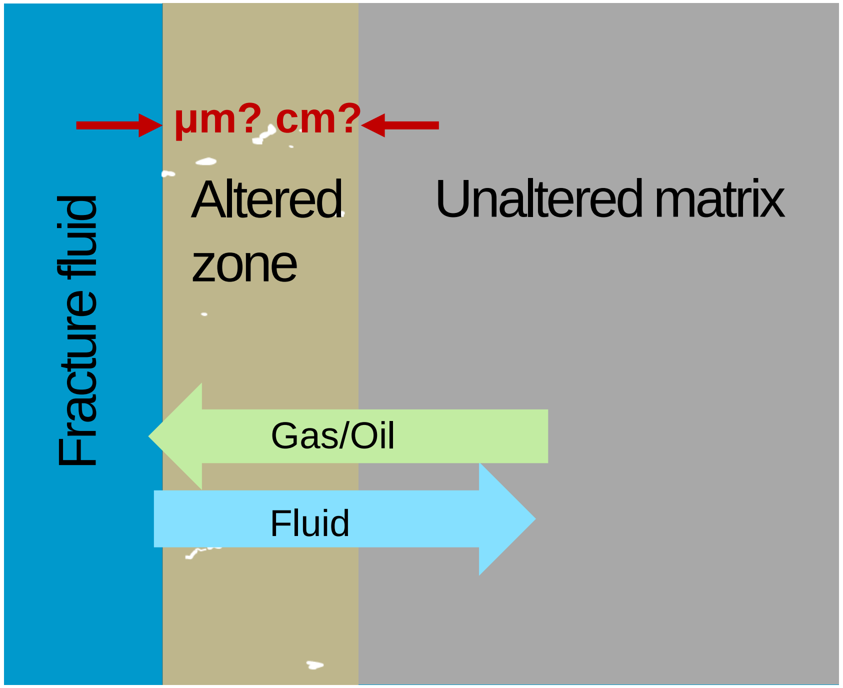
Noël

Result 1. Iron scale precipitation in Altered Zone

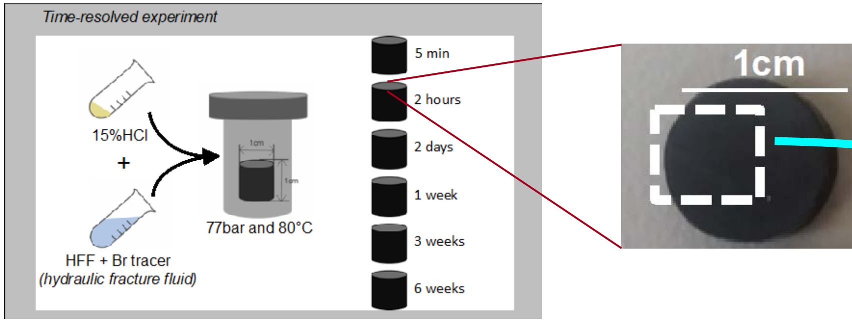
The problem: Scale precipitation in altered zone chokes hydrocarbon production

The questions:

- Reaction penetration depth?
- Controlling factors?
- How are matrix permeability & diffusivity affected?



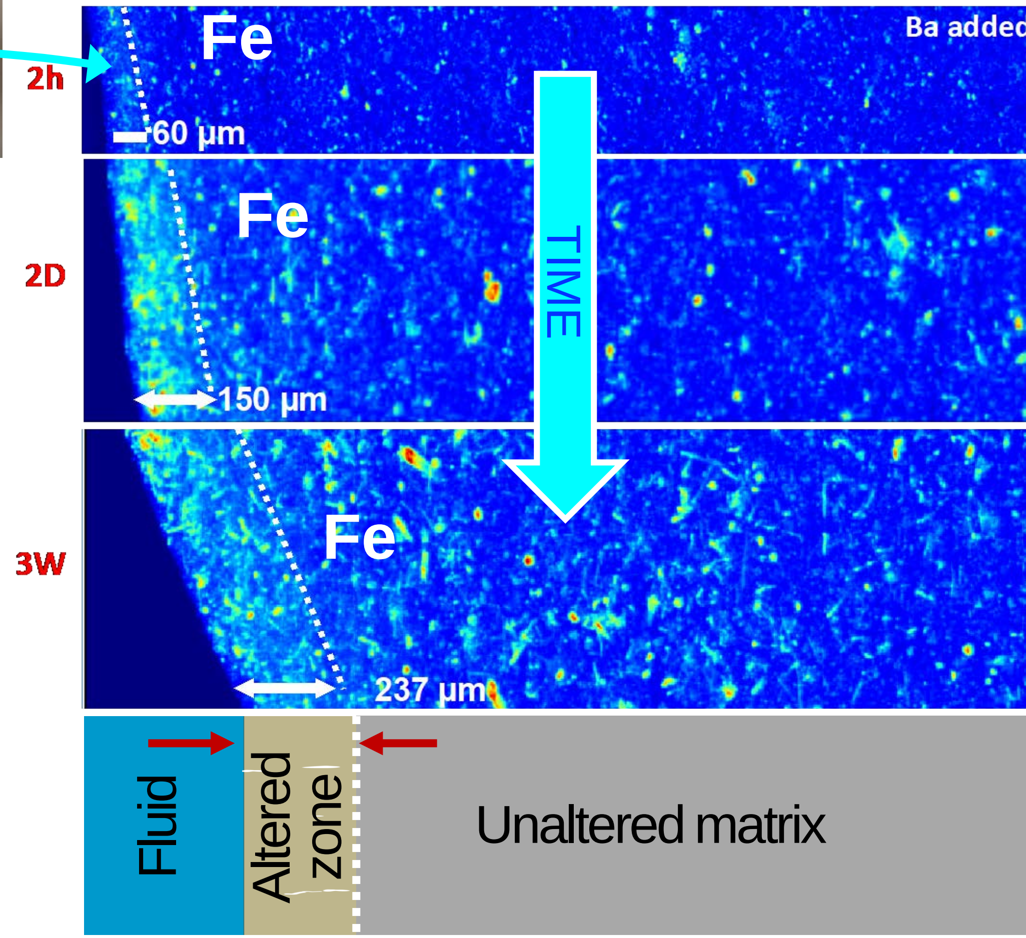
Result 1. Iron scale precipitation *time lapse*



XRF chemical mapping

Carbonate-poor Marcellus shale

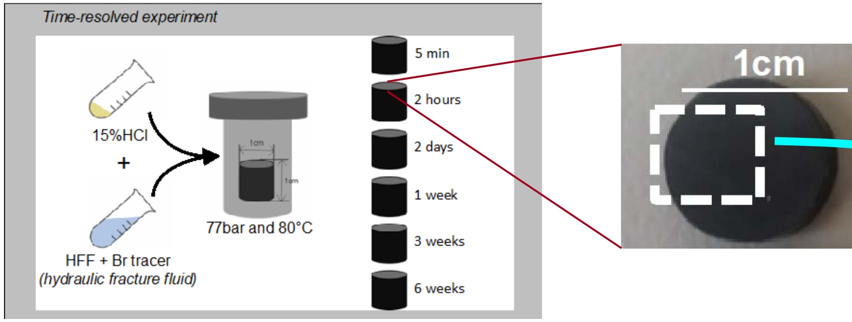
Fe mapping



- Time-lapse reactors cover *wide* range of chemical conditions.
- *Complements NETL work*
- Characterization:
  - Fe(III)-oxide scale thickens over time in spite of persistent acidic conditions (first time observed!)
  - Fe-rich *clay mineral scale* precipitated (first time observed!)

SLAC | NATIONAL ENERGY TECHNOLOGY LABORATORY | Office of Oil and Natural Gas

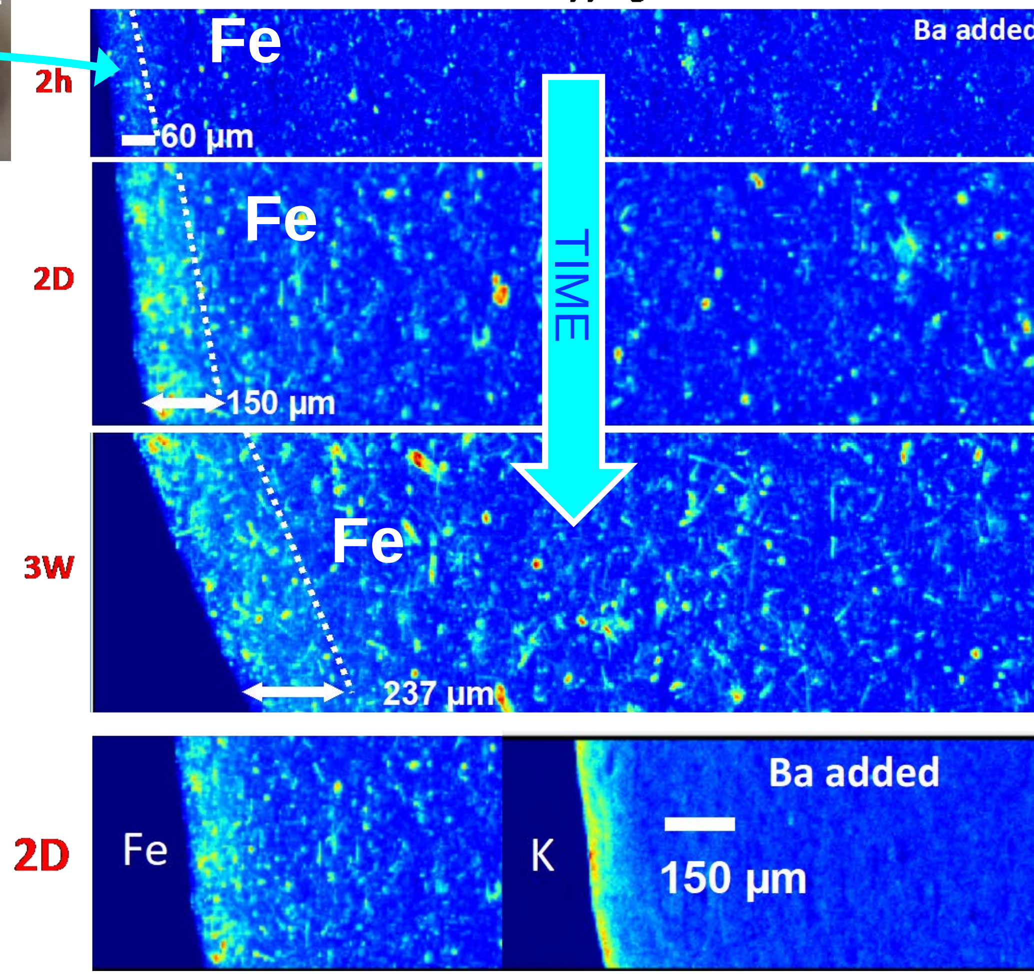
Result 1. Iron scale precipitation *time lapse*



XRF chemical mapping

Carbonate-poor Marcellus shale

Fe mapping



- Time-lapse reactors cover *wide* range of chemical conditions.
- *Complements NETL work*
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  - Fe-rich *clay mineral scale* precipitated (first time observed!)

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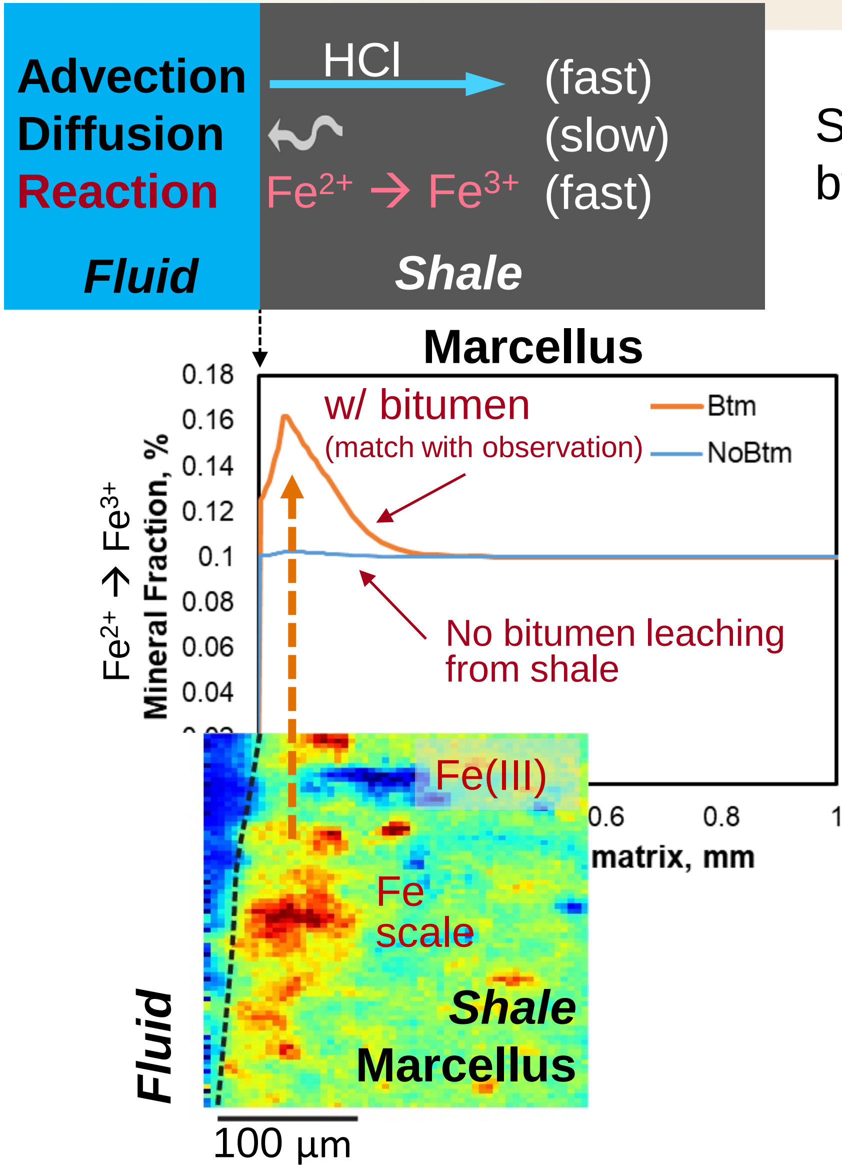
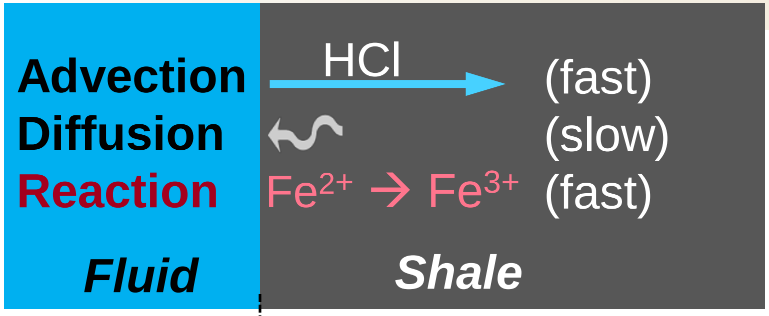
Result 2. Iron scale: Reactive transport modeling



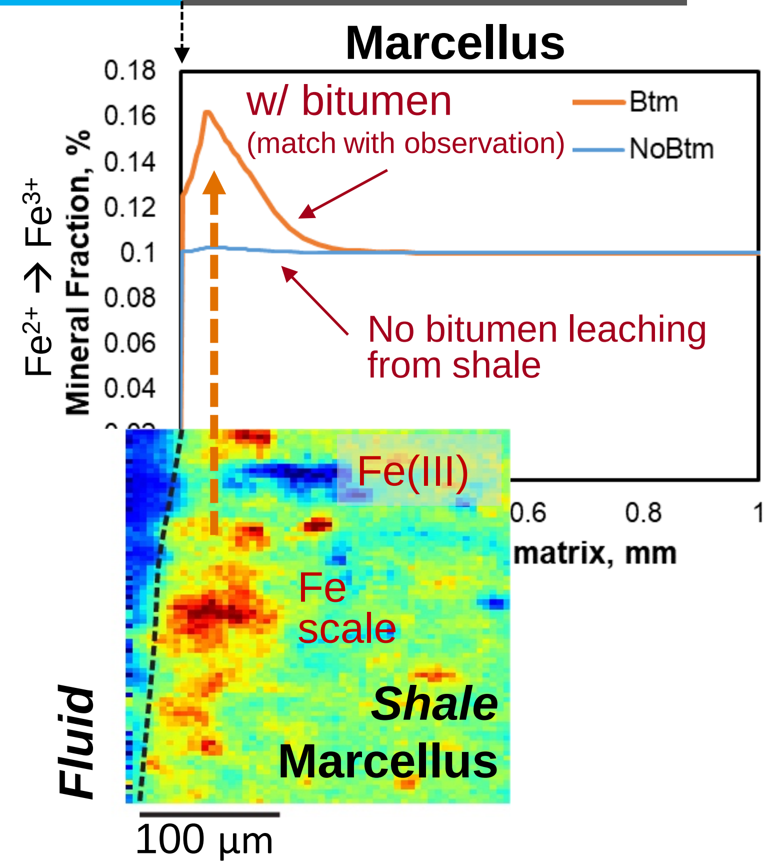
Simulated by model

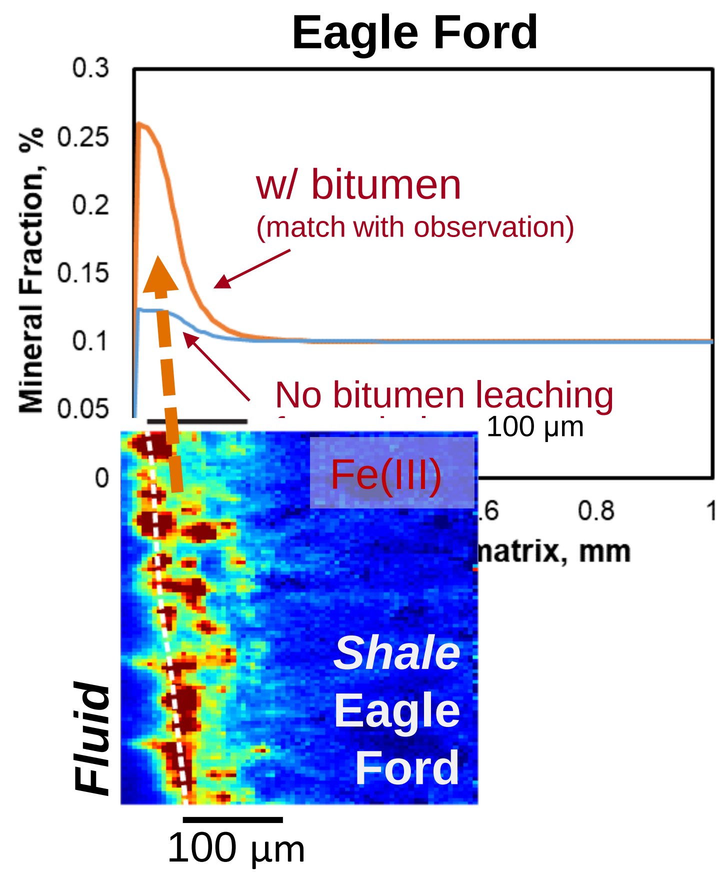
Li et al. *URTeC*, 2019

Result 2. Iron scale: Reactive transport modeling

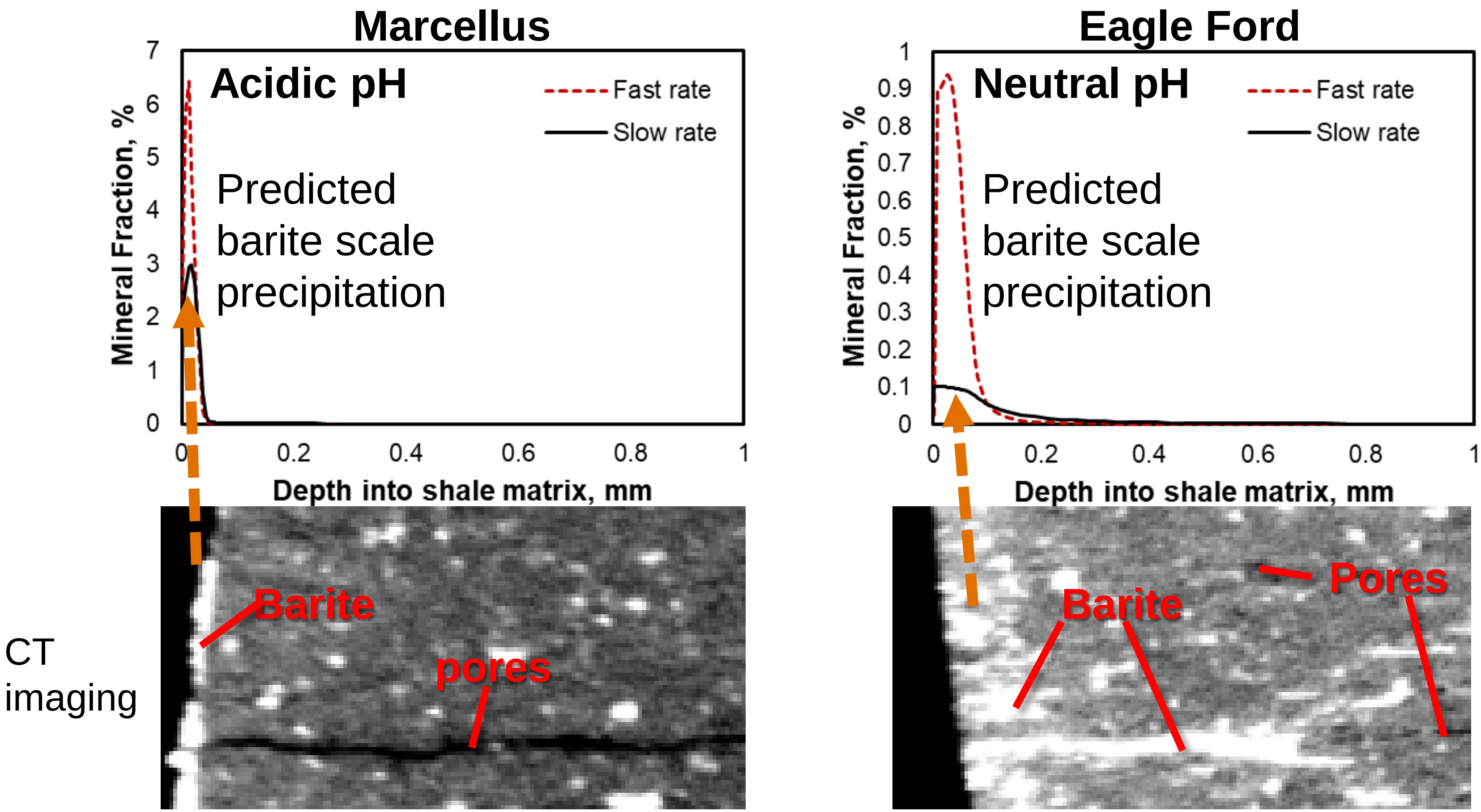


- Bitumen increases Fe(III) scale precipitation
- Predicted mitigation: Guar gum in frac fluid can adsorb Fe and reduce scaling





Result 3. Barite scale: Reactive transport modeling



- pH strongly affects rates – fast at acidic conditions
- Neutral pH: only slower rates can match with observations
- Barite suppressed by chemicals in the frac fluid

Reaction *rates* extremely important

…controlled by pH, fluid composition

Task 2: Scale Geochemistry

2.1 Scale prediction

What chemical parameters control scale in different basins?

2.2 Scale mitigation

Develop chemical strategies to mitigate scale.

Emphasize *incremental* optimization

2.3 In-situ scale monitoring

Can we monitor scale and fractures simultaneously?

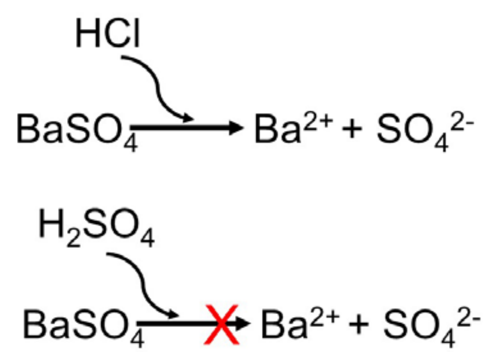
Result 4: Acid swap to control barite scale

The problem: *Ba release from mud*

- Drilling mud is rich in barium
- Ba dissolved by HCl can precipitate in reservoir
- NaCl *promotes* barite dissolution

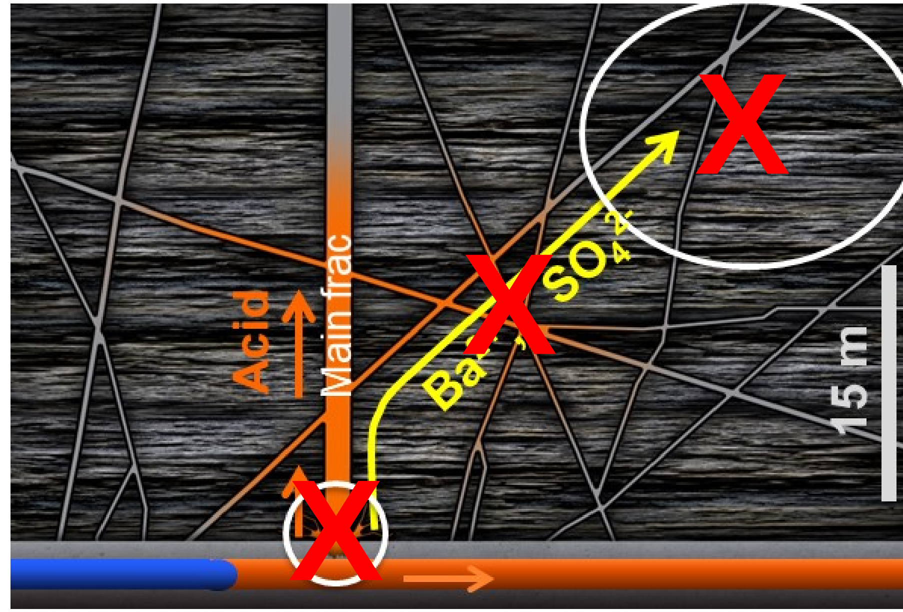
The solution: *acid swap*

- Modeling: H_2SO_4 *should* shut down Ba leaching *at the source*



- *But:* need to control $CaSO_4$ precipitation: Citrate *should* work

Jew et al. *URTeC*, 2019



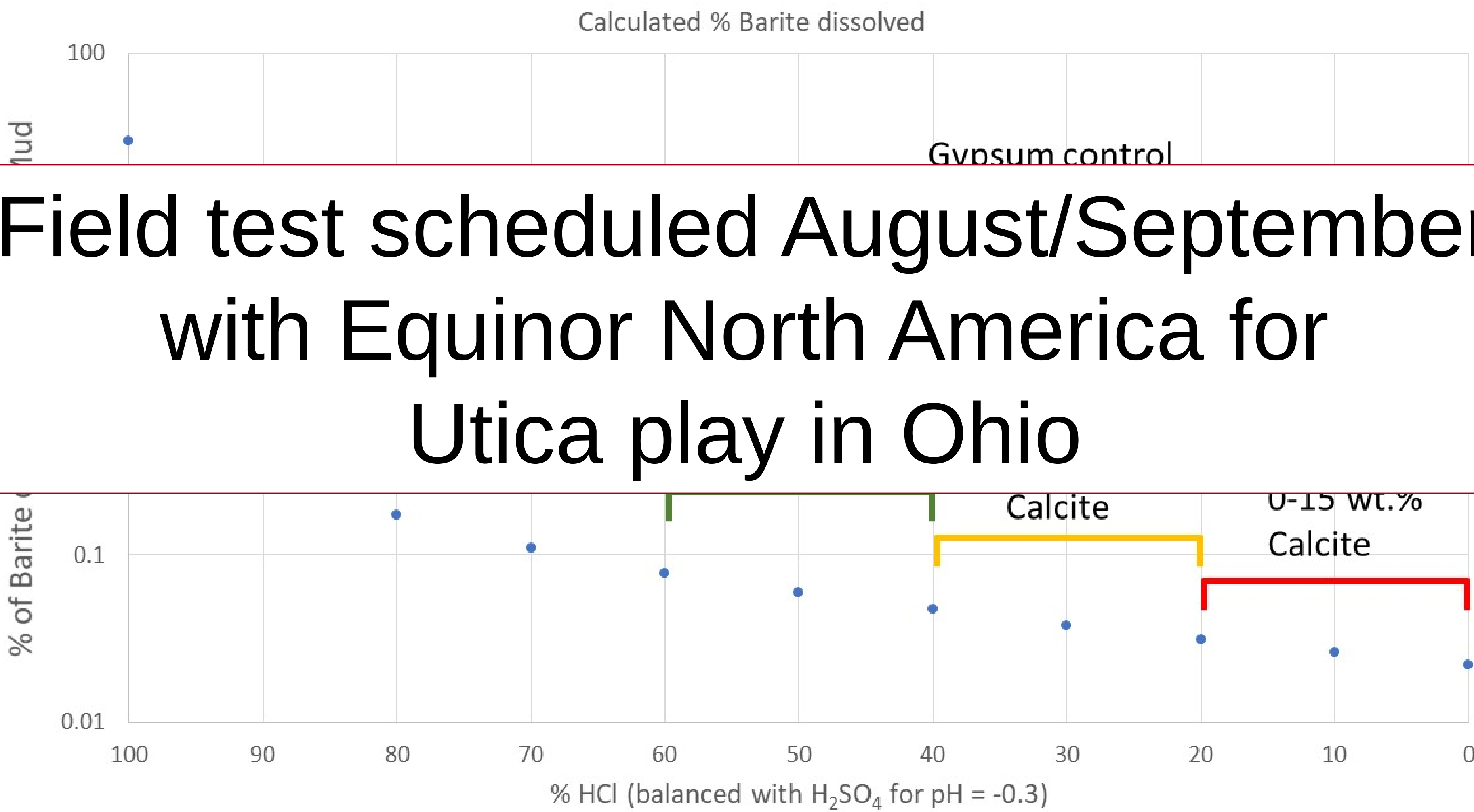
Barite dissolution

Ba transport to fractures

Precipitation in fracture system

Result 4. Lab tests suggest incremental acid swap works

Jew et al. *URTeC*, 2019



Field test scheduled August/September with Equinor North America for Utica play in Ohio

Model-based iron scale mitigation in 2020

Model–guided sensitivity analyses: ID most important parameters

↓

Use the model to optimize scale inhibitor usage

↓

Verify in laboratory experiments

Continue basin-specific experimental observations

Task 2: Scale Geochemistry

2.1 Scale prediction

What chemical parameters control scale in different ba

Vanorio

Ding

Clark

2.2 Scale mitigation

Stanford Geophysics

Develop chemical strategies to mitigate scale.

2.3 In-situ scale monitoring

Can we monitor scale and fractures simultaneously?

Next generation shale geochemistry needs:

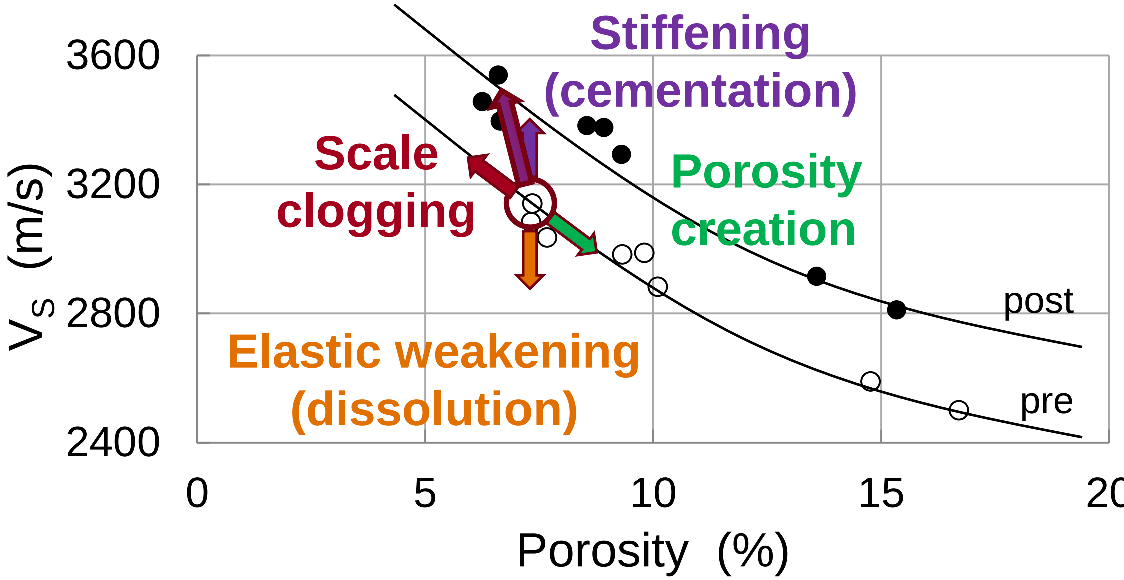
The Vision: ***In the field, in real time:***

Monitor and mitigate scale precipitation

… and optimize porosity and permeability

The problem: Currently no way to monitor these properties in the field!

The solution: Develop new acoustic-based technologies for shale geochemistry

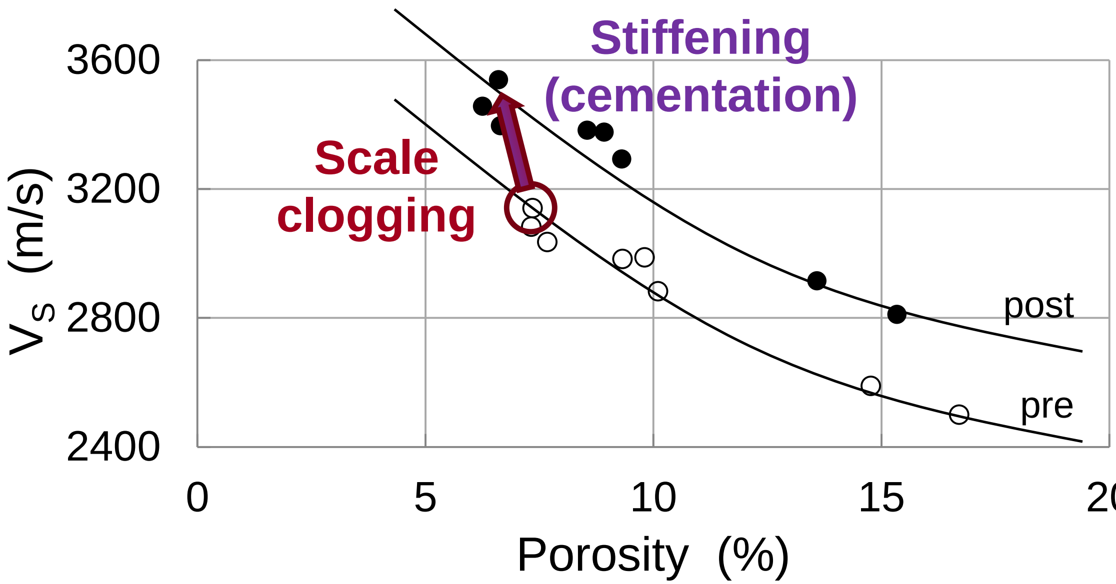


Vanorio et al., 2011

This example: 13% increase in V_S after salt Precipitation

Velocity-Porosity relationship for sandstones

S-wave velocity: Sensitive to mineral scale & porosity



Vanorio et al., 2011

This example: 13% increase in V_S after salt Precipitation

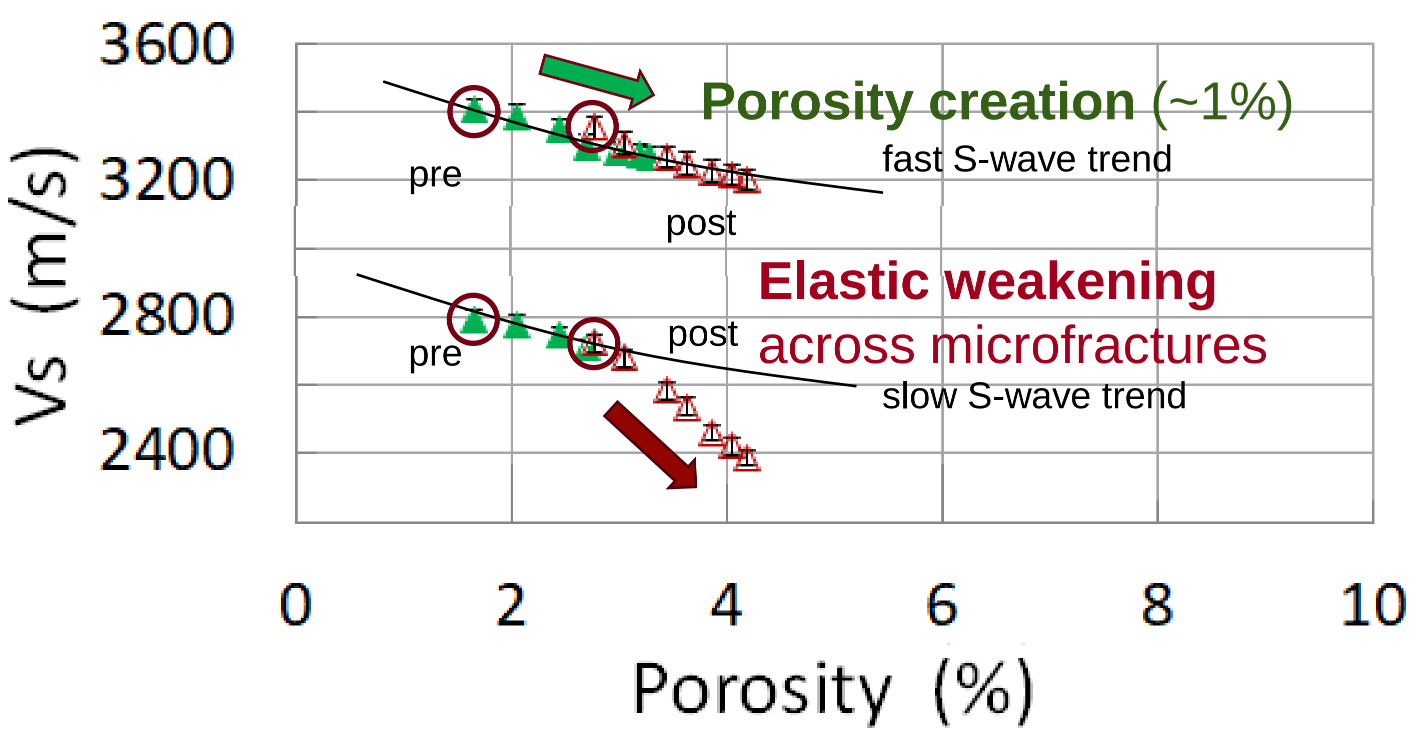
This approach *should* work well for shale.

Does it?...

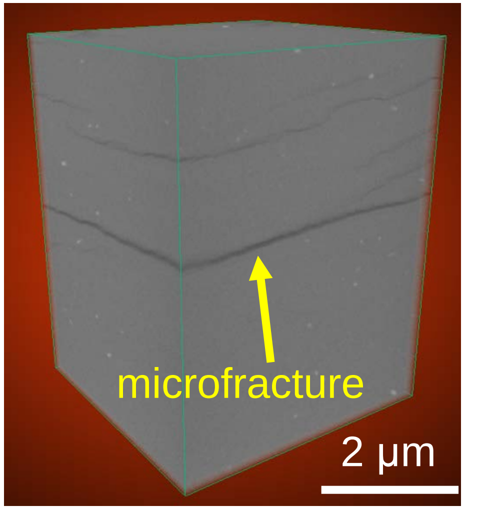
Result 5. Monitoring *multiple* dissolution processes

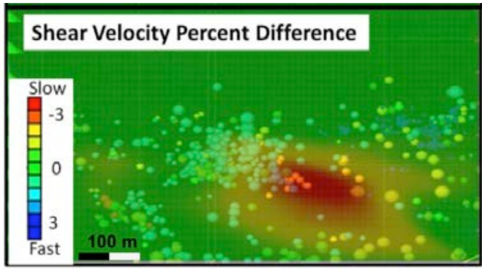
SLAC

Dissolution causes velocity decrease and S-wave splitting



Micro-CT Image





Marcellus Formation, PA
Rampton & Hammack, 2018

Detected and distinguished two different processes during first set of tests!

Highly relevant for field application!

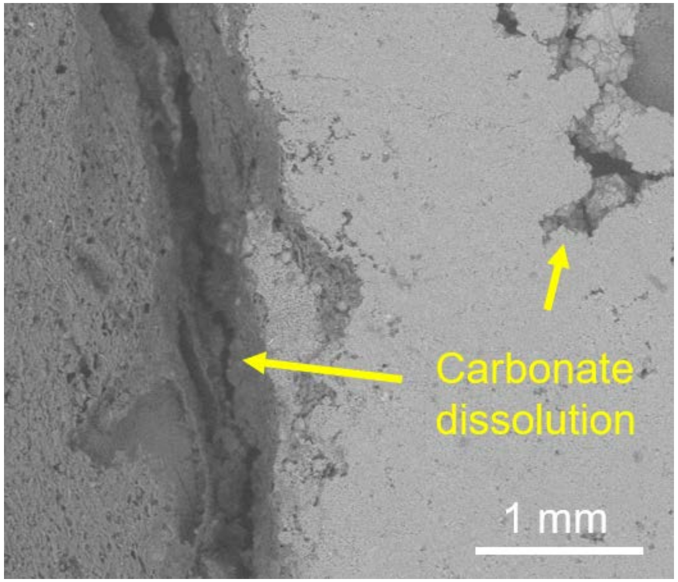
Future work: End-member scenarios

Investigate the acoustic signatures of dominant dissolution or scaling

Strong dissolution

HCl acid (pH<2),
reservoir condition

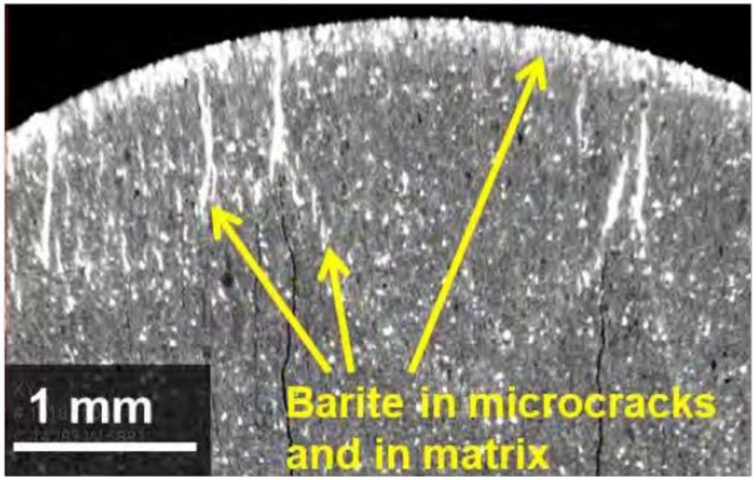
Porosity creation and elastic weakening



Strong scaling

HCl acid (pH~5),
$BaCl_2 + Na_2SO_4$,
reservoir condition

Pore clogging and cementation



Task 3: Optimize porosity

Systematically manipulate altered zone porosity to improve permeability

Kovscek

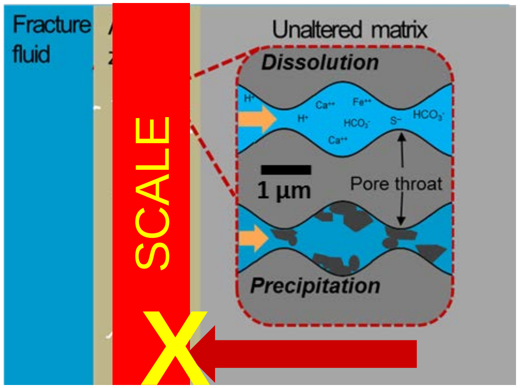
Gundogar

Stanford Energy Resources Engineering

Manipulation of matrix accessibility

The problem: Injection conditions are far from optimal for producing from matrix.

- Promotes scale formation
- Size of acid slug
- pH
- Salinity



Hydrocarbon

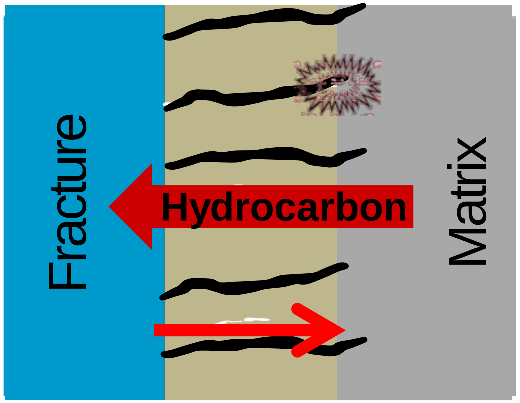
Manipulation of matrix accessibility

The problem: Injection conditions are far from optimal for producing from matrix

- Promotes scale formation
- Size of acid slug
- pH
- Salinity

Large *Damköhler*;
Fast reaction

Large *Peclet*;
Advection dominated



The solution: Manipulate chemistry & pressure to maximize *Damköhler*, *Peclet* numbers

- Promotes worm-holing across altered zone
- Provides target to ***translate lab results to the field***
- Avoid conditions that promote scaling

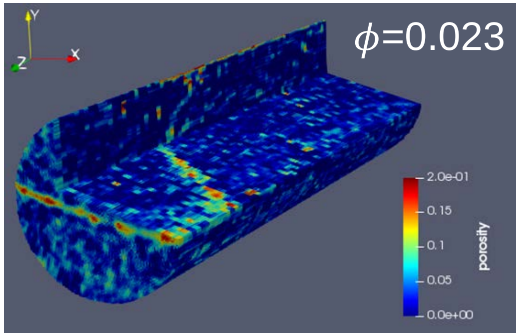
Damköhler = reaction rate / convection rate

Peclet = convection rate / diffusion rate

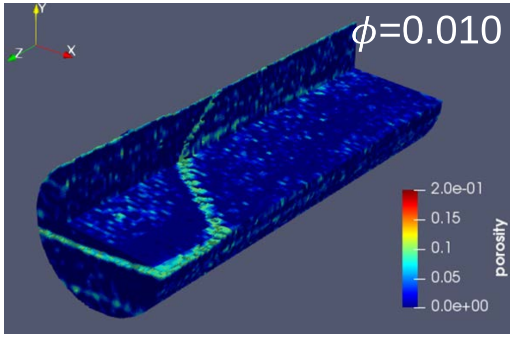
Result 6. Core-flood permeability decreases w/porosity

3D Porosity reconstructions using fluid substitution with Krypton (large x-ray attenuation)

Before stim fluid injection



After stim fluid injection



Brine (0.5 M NaCl) injection: Perm: 7.12 uD

HFF (pH 2.0) injection: Perm: 1.21 uD

- **Decrease in porosity of both matrix & fractures**
- **Lower effluent volume during HFF injection**
- **Clay or iron scale precipitation? Clay swelling?**
- SEM/EDS/XRF analysis of shale fabric in progress

Currently combining our findings with those from **other subtasks** to determine the dominant factors

Ongoing work

Develop manipulation strategies that enhance matrix accessibility using

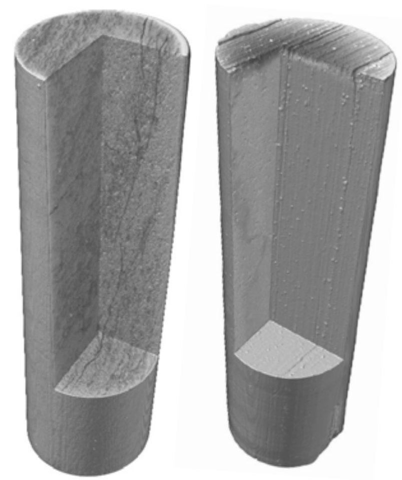
- Chemical hypotheses from Task 2, prior
- Flow-through-matrix core floods guided by brine and HFF from **Task 2.1-2.3**
- In situ porosity maps from CT
- Multiscale image analysis to highlight changes to shale fabric

⬇

Reactive transport simulations (Pe ≈100) guided by Task 2.1.2

- to better analyze experiments
- to scale from laboratory to field

Bone Spring top and bottom outcrop cores

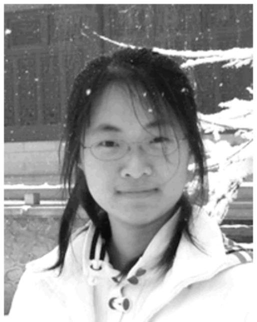


Marcellus carbonate- and clay-rich cores from MSEEL

Team

SLAC

Li



Geochemical modeling

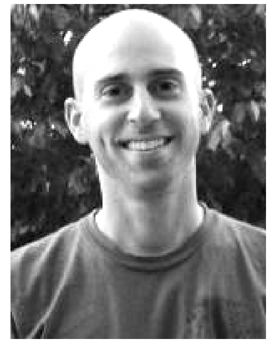
Spielman-Sun

Experimental geochemistry

Ding

Rock physics

Clark



Rock physics

Gundogar

Fluid transport

Noël

Experimental geochemistry

Bargar

Experimental geochemistry

Jew

Experimental geochemistry

Maher

Geochemical modeling

Kovscek

Fluid transport

Vanorio

Rock physics

Brown

Experimental geochemistry

Thank you!

U.S. DEPARTMENT OF ENERGY
Office of Fossil Energy

Office of Oil and Natural Gas

Project Management slides

Major Accomplishments to date

- ✓ Published 11 manuscripts; 1 in review; 2 in preparation
- ✓ 1 Patent on acid-swap technology for barite scale mitigation
- ✓ 27 presentations (4 invited) at national/international meetings
- ✓ Work with 2 industrial partners to use new scale mitigation knowledge in industrial practices
- ✓ Field testing barite scale mitigation practices
- ✓ Discovered/quantified organic-mediated Fe oxidation and scale precipitation mechanisms
- ✓ Introduced new technologies for unconventional geochemistry monitoring

Lessons learned

- 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

Synergies & Synergy Opportunities

Existing collaborations:

• Fracture-scale geochemistry	NETL (A. Hakala, C. Lopano)
• Deep-water offshore	NETL (I. Gamwo)
• Field laboratories	MSEEL, HFTS
• Multi-length scale research	LBNL (Steefel, Deng), LLNL (Morris)
• Industrial partnerships	Pioneer Natural Resources
	Equinor North America
• Academic partnerships	Penn State (S. Lvov, D. Hall)

New collaborations we are pursuing:

• Neutron scattering on shale systems	LANL (H. Xu)

Project Summary

SLAC

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

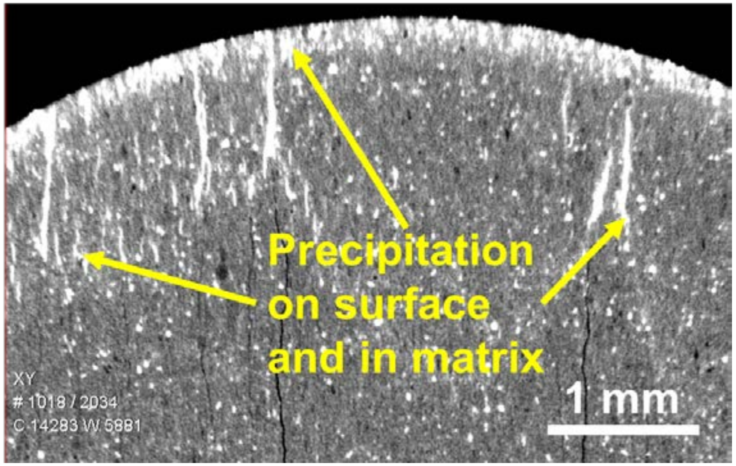
Appendices

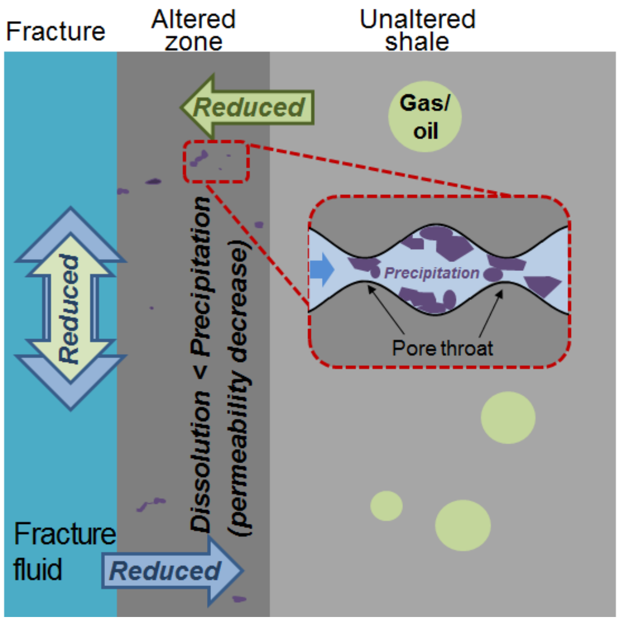
Benefit to the Program

Program goals addressed:

- Improve ***recovery factors***
- Improve *water reuse/recycling*
- Lay foundation for *next generation geochemical control* of subsurface mineral scale and porosity
- Lay foundation for *transformational advancement* of unconventional resource recovery

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
- Interactionions with industry
- Patent fiilings

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 *Geochemistry*	Eleanor Spielman-Sun
Task 2.2:	Kate Maher *Reactive transport*	Qingyun Li
Task 2.3:	Tiziana Vanorio *Rock physics*	Jihui Ding
Task 3.0:	Tony Kovscek: *Fluid flow, reservoir engineering*	Asli Gundogar

Gantt Chart

Bibliography

Patents

Patent (2019)- Fracture Fluid Alteration to Mitigate Barite Scale Precipitation in Unconventional Oil/Gas Shale Systems. Patent ID: 62/717326

Journal Publications

Jew, A.D., Li, Q., Cercone, D., Brown, G. Jr., Bargar, J. 2019 A New Approach to Controlling Barite scaling in Unconventional Systems. Unconventional Resources Technology Conference Proceedings, 512. DOI 10.15530/urtec-2019-512

Li, Q., Jew, A.D., Cercone, D., Bargar, J., Brown, G. Jr., Maher, K. 2019 Geochemical Modeling of Iron (Hydr)oxide Scale Formation During Hydraulic Fracturing Operations. Unconventional Resources Technology Conference Proceedings, 612. DOI 10.15530/urtec-2019-612

Li, Q., Jew, A.D., Kiss, A., M., Kohli, A., Alalli, A., Kovscek, A.R., Zoback, M.D., Cercone, D., Maher, K., Brown, G. Jr., and Bargar, J. 2019 Thicknesses of chemically altered zones in the shale matrices from interactions with hydraulic fracturing fluid. Energy & Fuels. DOI https://doi.org/10.1021/acs.energyfuels.8b04527

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Basin-specific water formulations

SLAC

- ‘Fresh’ and ‘reuse’ water formulations

Midland, TX

Ingredient	Concentration (% mass) excludes proppant
Water	98.30879874
Cupric Chloride	0.000213507
Thioglycol	0.002314867
Methyl Alcohol	0.040026969
Kerosene	0.202809304
C-11 to C-14 alkanes	0.001663108
Propylene pentamer	0.052522755
Methyl Alcohol	0.010506799
2-Butoxyethanol	0.030632655
Ammonium Persulfate	0.083425104
Gluteraldehyde	0.010473087
Methanol	0.006281605
Polyphosphonic acids	0.006629958
Isopropanol	0.006888414
Propargyl Alcohol	0.006888414
Methanol	0.006888414
Isooctyl Alcohol	0.006888414
Xylene	0.006888414
15% Hydrochloric acid	
Also known as 2-mercapteoethanol	
Also known as polyphosphoric acid	
Also known as 2-ethyl-1-hexanol	

Reeves Co, TX

Ingredient	Concentration (% mass) excludes proppant
Water	97.10902243
Guar gum	0.17765487
Amorphous silica	0.000893534
Glutaraldehyde	0.014138192
Methanol	0.014138192
Ammonium perulfate	0.008743058
Potassium metaborate	0.135692715
Potassium hydroxide	0.013436938
Ethylene glycol	0.013436938
Potassium hydroxide	0.010643231
2-butoxyethanol	0.020992388
2-propanol	0.020992388
Acetic acid	0.004309321
Citric acid	0.002578806
Methanol	0.003766414
Propargyl alcohol	0.000757807
Ammonium perulfate	0.0085734
15% Hydrochloric Acid	

MSEEL

Ingredient	Concentration (% mass) excludes proppant
Water	99.70400729
Ammonium sulfate	0.017144809
Acrylamide*	0.012636612
Glutaraldehyde	0.0043602
Guar gum	0.003130692
Polymer 2-acrylamido-2-methylpropanesulfonic acid	0.001354736
Ethanol 2,2',2''-nitrilotris 1,1',1''-tris(dihydrogen phosphate)	0.001935337
Sodium erythorbate	0.000831056
Urea	0.000831056
Alkyl(c12-16) dimethylbenzyl ammonium chloride	0.000774135
Trisodium ortho phospate	0.000580601
Methanol	0.000466758
Fatty acids, Tall-oil	0.000295993
Thiourea polymer with formaldehyde and 1-phenylethanone	0.000250455
Sodium sulfate	0.000193534
Ethylene glycol	0.000170765
Ethoxylated alcohols	0.000113843
Ethanol	9.10747E-05
Propargyl alcohol	7.96903E-05
2-Propenamid	4.55373E-05
Hexadec-1-ene	2.27687E-05
Tetrasodium EDTA	2.27687E-05
Diammonium peroxidusulphate	1.13843E-05
1-Octadecene	1.13843E-05
15 % Hydrochloric Acid	

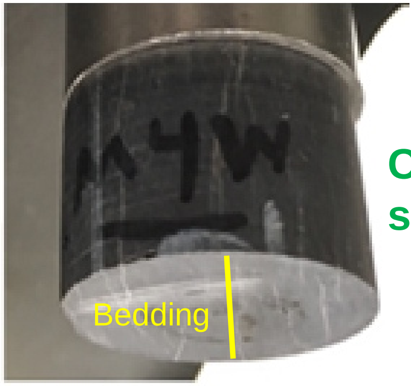
Basin-specific stimulation recipes

MSEEL **Midland, TX**

MSEEL					Midland			
Fluid	Time	Volume	%		Fluid	Time	Volume	%
7.5% HCl	4.2	[illegible]	[illegible]		[illegible]	[illegible]	24	0.34
Slickwater	21.5	[illegible]	[illegible]		[illegible]	[illegible]	1143	16.14
Slickwater	3.2	[illegible]	[illegible]		[illegible]	[illegible]	595	8.40
Slickwater	3.4	[illegible]	[illegible]		[illegible]	[illegible]	595	8.40
Slickwater	4.6	[illegible]	[illegible]		[illegible]	[illegible]	560	7.91
Slickwater	5.8	[illegible]	[illegible]		[illegible]	[illegible]	500	7.06
Slickwater	9	[illegible]	[illegible]		[illegible]	[illegible]	500	7.06
Slickwater	6.2	23949	6.67		Slickwater	6	500	7.06
Slickwater	5.8	23959	6.68		Slickwater	6	537	7.58
Slickwater	4.6	18528	5.16		Slickwater	7	571	8.06
Slickwater	4.6	18527	5.16		Slickwater	7	524	7.40
Slickwater	8.3	32388	9.03		Slickwater	7	570	8.05
Slickwater	24.5	92451	25.76		Slickwater	6	461	6.51

All tasks using common shale sources, fluids & stimulation sequences

Workflow for a basin-specific approach



Carbonate-rich sample (31 wt.%)

Samples

1” Marcellus well cores

Pre-reaction characterization

porosity, permeability, velocity, μ-CT/SEM

Reaction

basin fluid, reservoir conditions

Post-reaction characterization

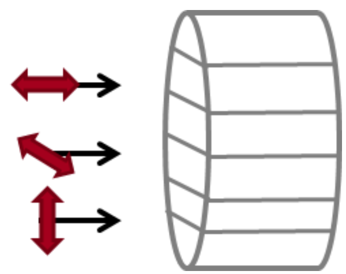
fluid chemistry analysis

No-carbonate sample (~ 0 wt.%)

P-wave

fast S-wave

slow S-wave
(sensitive to bedding)



- 40 ml frac fluid
- 0.13 wt.% HCl
- 78 bar, 80°C, 3 weeks
- **pre pH~2, post pH~5**

Workflow: optimize for FLOW across altered zone

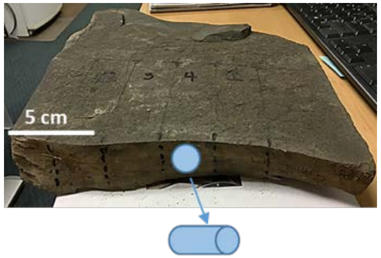
Workflow

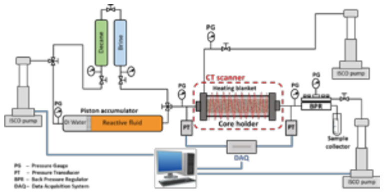
Prepare cores
- parallel to bedding planes

React with fluids
- Core flood flow through
- Monitor w/CTCT

Characterize before & after
- whole core µCT
- CT/SEM/EDS
- He pyc., MIP, XRD
- Effluent fluid chemistry

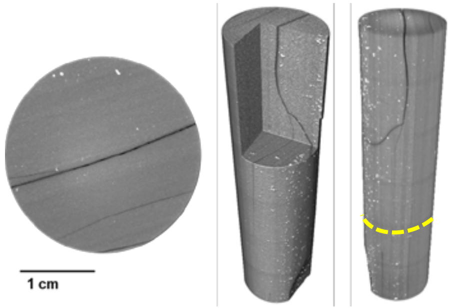
Marcellus outcrop (1” dia x 3” long)

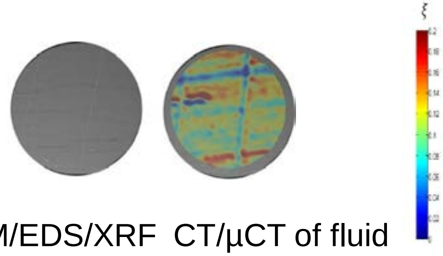




Pre-Vacuum → Kr Inj → Re-Vacuum → Brine Inj → HFF Inj (at 80°C)

Shale fabric characterization using multiscale/multimodal imaging





SEM/EDS/XRF Mosaic

CT/µCT of fluid penetration

* Light areas are more dense.

(Aljamaan et al., 2017)