Pore Scale Control of Gas and Fluid Transport at Shale Matrix-Fracture Interfaces

FWP 100211

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U.S. Department of Energy

National Energy Technology Laboratory

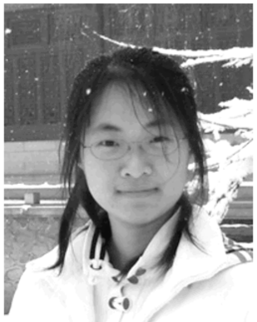
Mastering the Subsurface Through Technology, Innovation and Collaboration:

Carbon Storage and Oil and Natural Gas Technologies Review Meeting

August 15, 2018

Team

Li



Geochemical modeling

Jew

Experimental geochemistry

Dustin

Experimental geochemistry

Alalli

Geo-mechanics

Kohli

Geo-mechanics

Kiss

Imaging, CT

“Senior” personnel

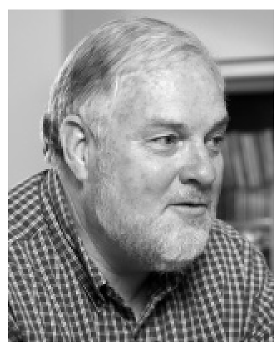
Maher

Geochemical modeling

Bargar

Experimental geochemistry

Brown

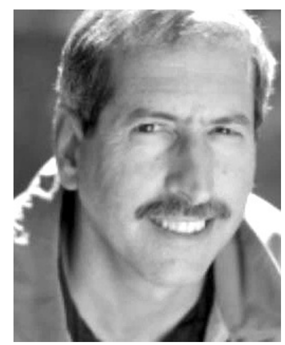


Experimental geochemistry

Kovscek

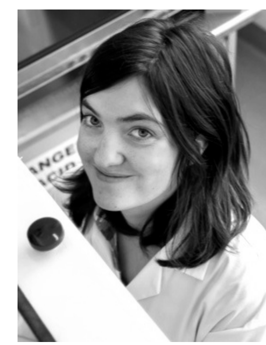
Fluid flow porous media

Zoback



Geo-mechanics

Harrison



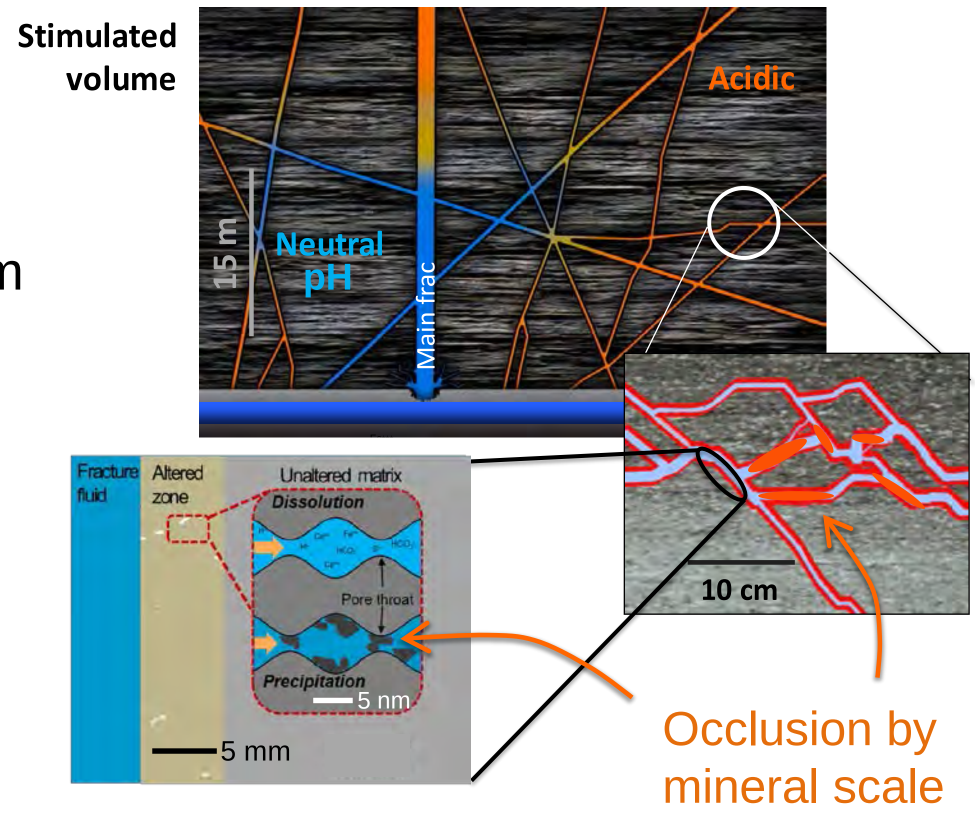
Geochemical modeling

Outline

- **Motivation and need**
- **Technical progress**
  - **Barium sources for barite scale formation**
  - **Geochemical controls for barite scale formation**
  - **Alteration of shale-fracture interfaces**
- **Accomplishments to date**
- **Lessons learned**
- **Synergy opportunities**
- **Project summary**
- **Appendix**
  - **Benefit to program**
  - **Project overview**
  - **Organization chart**
  - **Gantt chart**
  - **Bibliography**

Mineral Scaling in Stimulated Rock Volume

- Low Recovery in Unconventional Gas/Oil
  - Gas: < 25%
  - Oil: < 10%
- Mineral scaling is a major problem
  - Mineral scaling occurs on multiple spatial scales
  - Large spatial range
  - Several forms (barite, iron, halides, gypsum)
- Reduced production and permanent formation damage



Reactive components

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Fluid components

Acids
- Hydrochloric acid

Oxidants
- Oxygen
- Ammonium persulfate

Inorganics
- Barium
- Calcium/Magnesium
- Iron
- Sulfate/sulfide

Organics
- Organic additives
- Natural organics
  - Bitumen
  - Acetate
  - Citrate

Dissolution

Precipitation

Mediate RATES

Shale

- Carbonates
- Pyrite
- Clays
- Tectosilicates

- Secondary minerals
- Scale minerals

- pH
- Ionic strength
- Mineral surfaces

Barite: one of most important scale minerals

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Barium ubiquitous in hydraulic fracturing systems

- > 1 g/kg oil/gas shales
- Generally supersaturated in flowback (e.g., Dieterich *Fuel* 2016)

Low solubility ($K_{sp} = 10^{-9.34}$)

Numerous sources of Ba:

- Ba-infused drilling mud (> 10 g/kg)
- Shale (> 1 g/kg): Barite, witherite, clays

(Renock, *Appl. Geochem*. 2016)

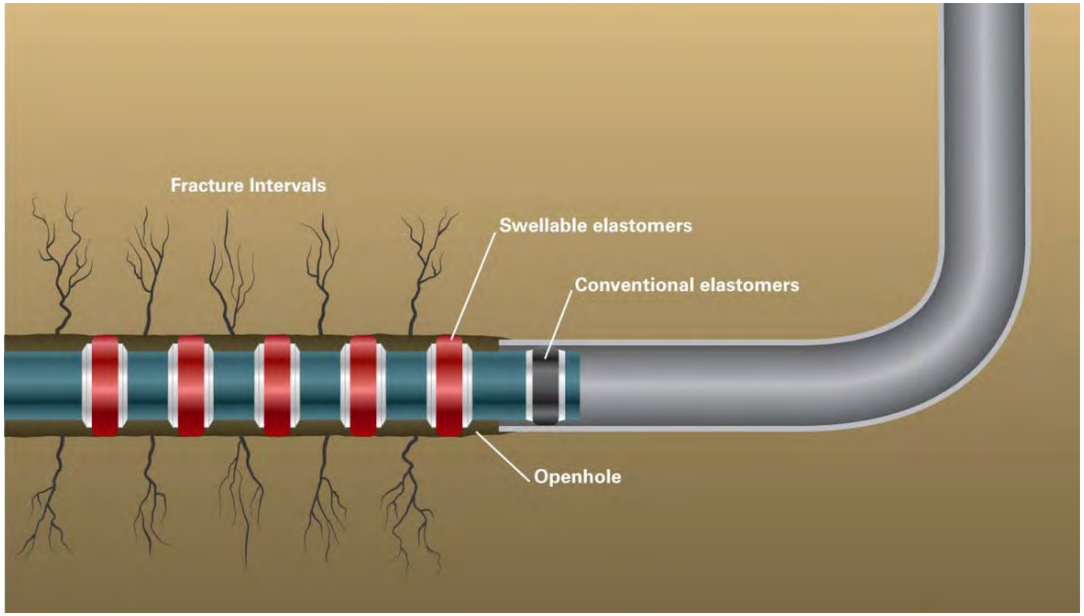
Technical progress

Major Questions Regarding Ba-scale

- Where is the majority of Ba coming from?
- What are the major reactions that affect Ba release?
- How is the rate and extent of barite scale precipitation impacted by:
  - Inorganic and organic constituents?
  - Shale mineralogy?

Possible Ba sources

- Base fluid (fresh water/brine)
- Additives
- Host shale
- Drilling mud
- Casing material

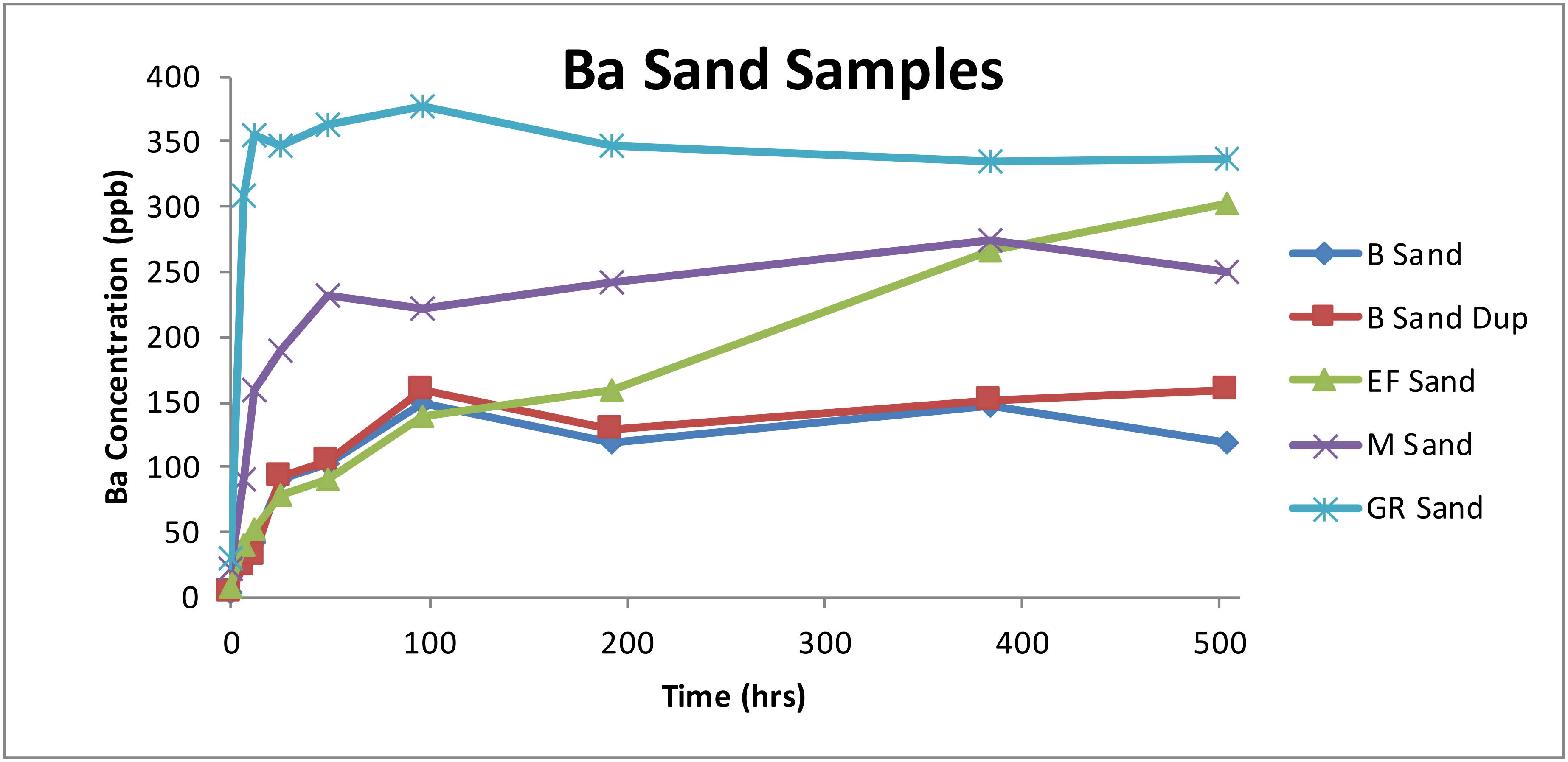


http://www.enventuregt.com/en/products-solutions/life-well/completions/multi-stage-fracturing

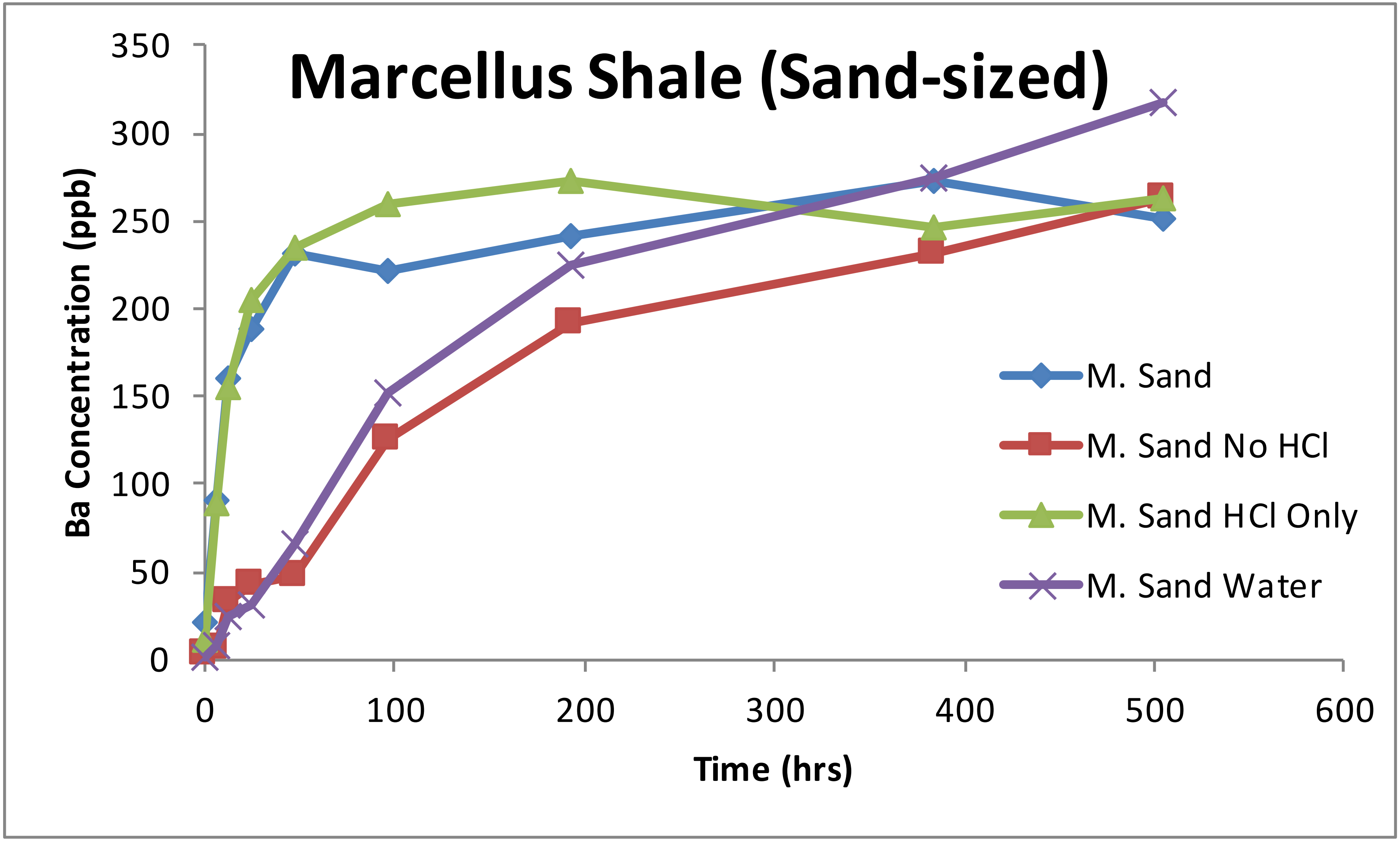
Is the shale the Ba source?

- Eagle Ford, Green River, Marcellus, Barnett
- Acidic Fracture fluid (pH = 2), water, pH 2 only, additives only
- Whole rock/ground
- 3-weeks at 80^{o}C

Ba release from different shales



Effect of solution chemistry on Ba Release



Ba release: Shale

- For high-clay shales, ~50% of Ba can be removed by acidic solutions
- Water alone can remove as much Ba from shale as acidic water, just slower
  - This suggests a portion of Ba in the shale is fairly soluble
- Ba release is fairly rapid with most occurring < 1.5 weeks under non-briny conditions

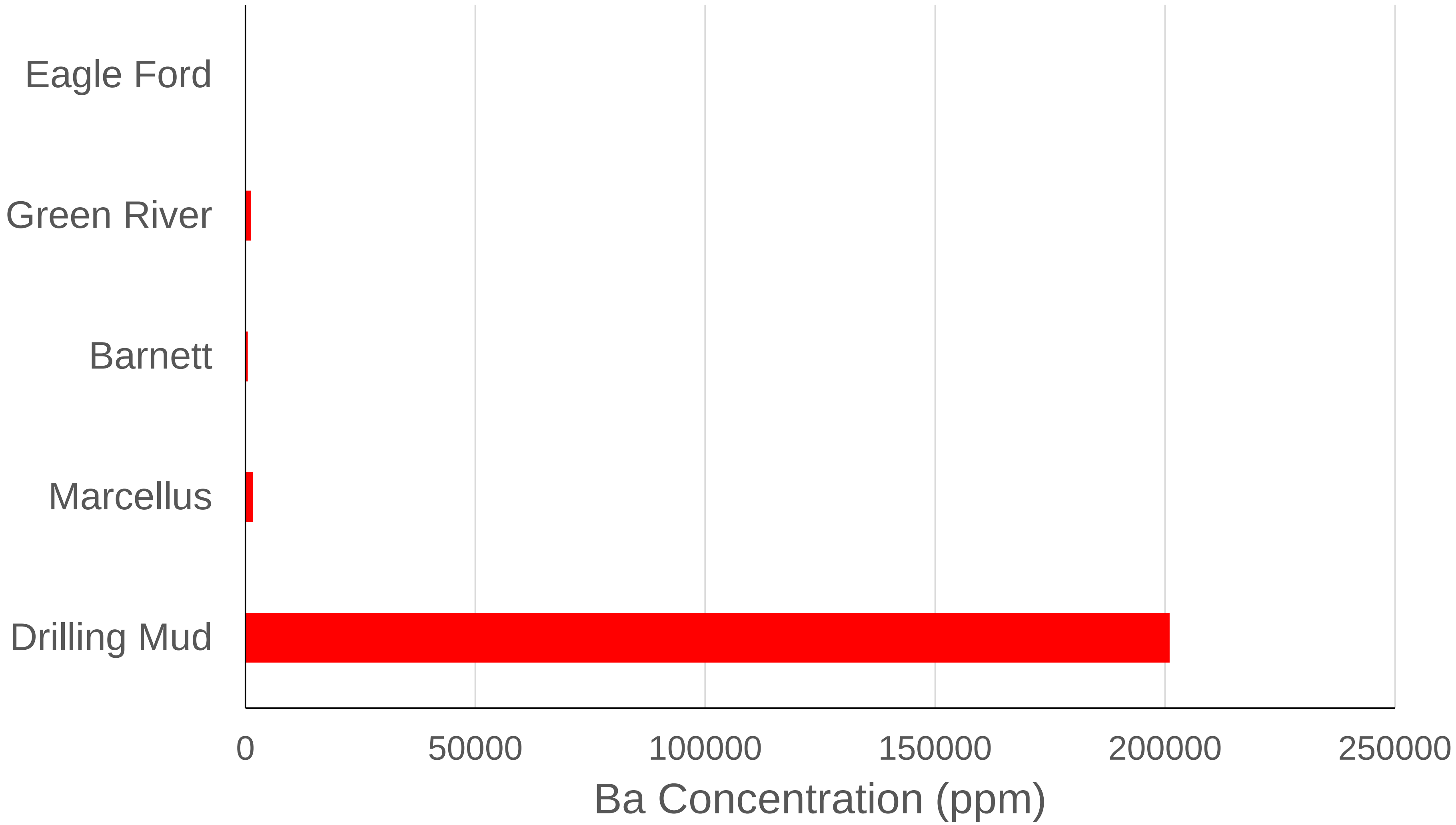
Shale	Ba Pre-reaction (ppm)	Ba Post-reaction (ppm)
Marcellus	1675	898
Barnett	518	215.7
Green River	1188	1094
Eagle Ford	104.8	< 1.5

What about Drilling Mud?

- Used to prevent blowout
- DM used at MSEEL site
- High density: ρ = 1.32 g/mL
- Density primarily due to barite
- NaCl concentration (soln.) ~111 g/L
- Ba concentration (soln.) 2 ppm
- 99.4% of all Ba in solids

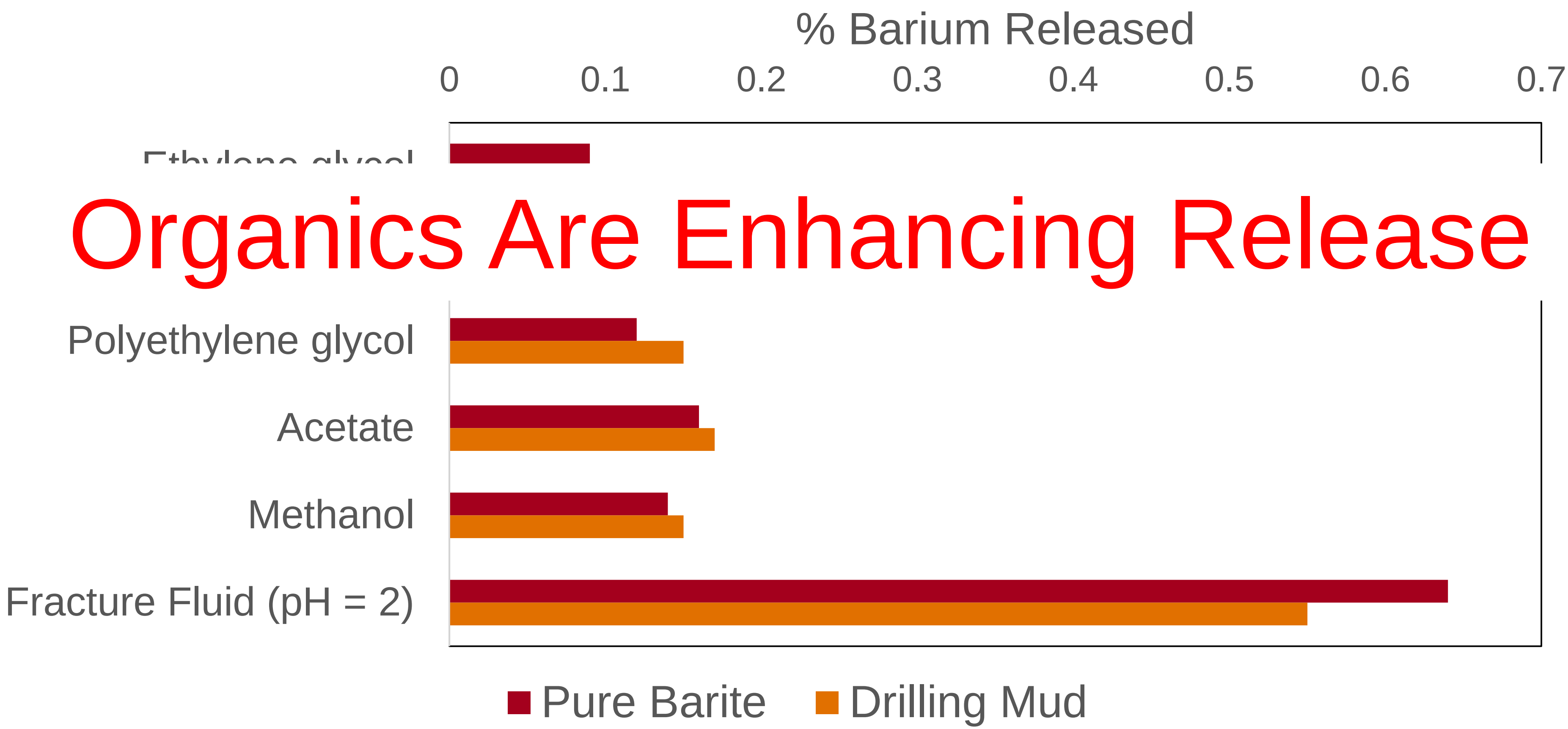
Same Mass

Comparison on Ba concentrations



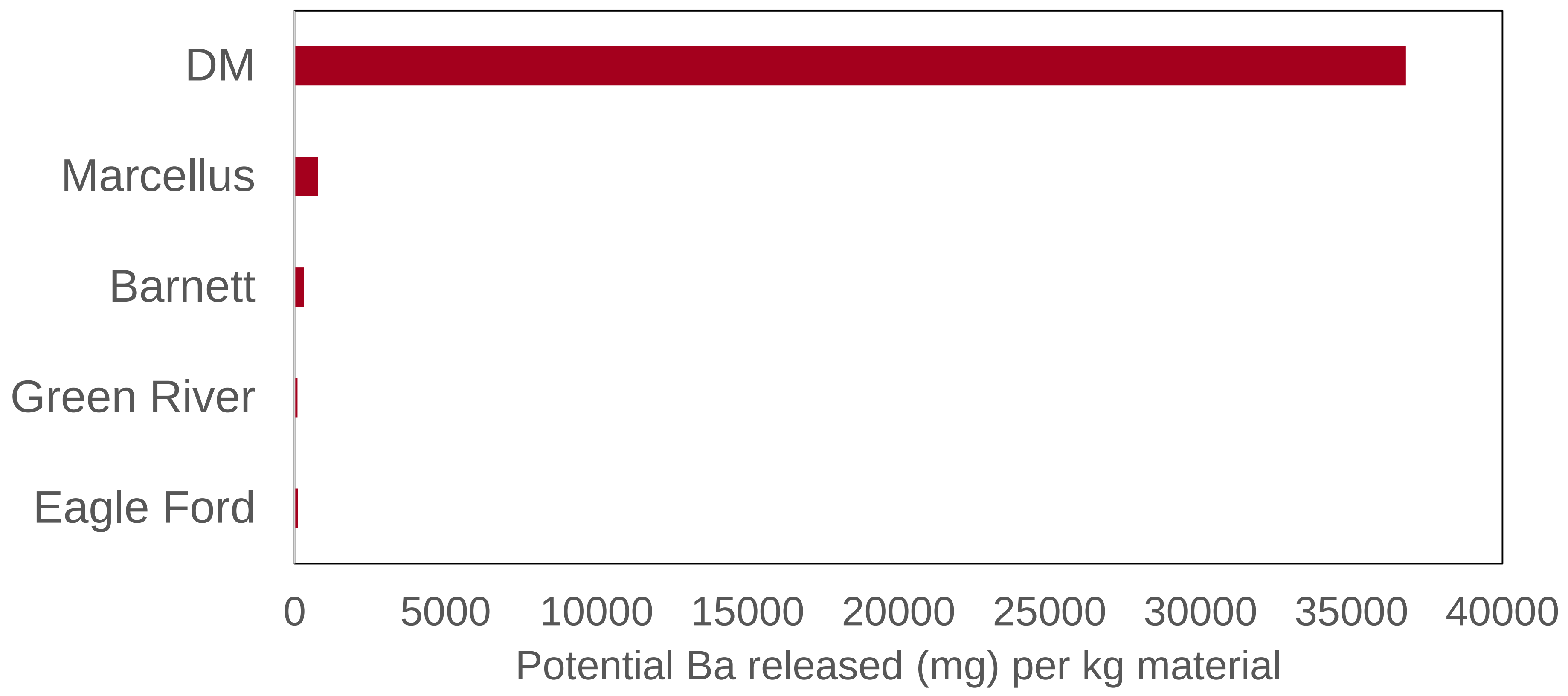
Ba Leach results pH and I.S.

Ba Leach results Organics



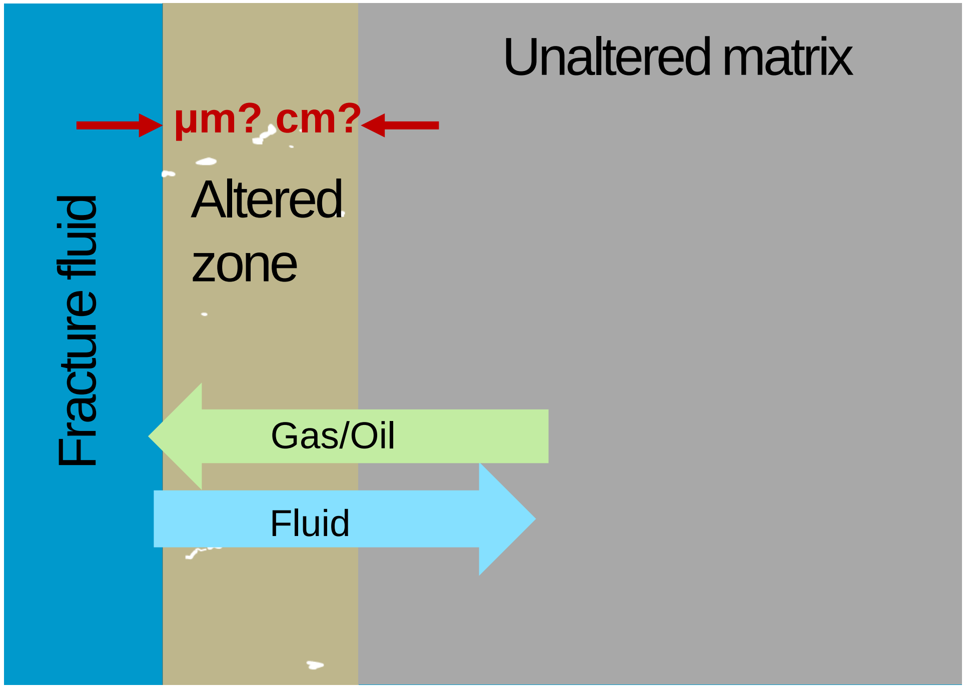
Organics Are Enhancing Release

Comparison: DM vs Shale (pH = 0)

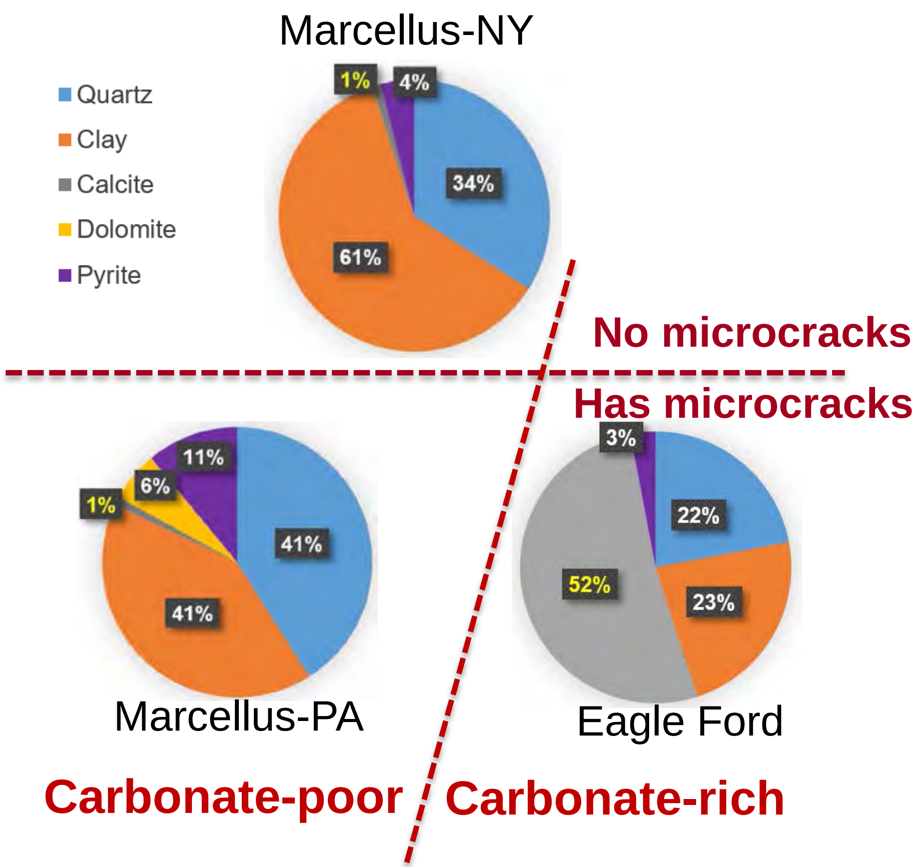


Impact of Barite precipitation on Altered Zone

- How deep can these chemical reactions penetrate the matrix?
- What are the controlling factors?
- How do these reactions affect matrix diffusivity/permeability?



How does shale mineralogy affect Ba-scale? Experimental approach



Synthetic fracture fluid (FF)

Ingredient	Mass	Purpose
Pure Water (contains dissolved O_2)	99.8%	Base fluid
Hydrochloric Acid	0.12%	Acid
Organics	<0.1%	Gellant, friction reducer, scale inhibitor, corrosion inhibitor, etc.

Condition 1: FF

Condition 2: FF + 2 mM $BaCl_2$ + 0.06 mM Na_2SO_4

SI(barite) = $\log_{10}(Q/K) = 1.3$

Barite ($BaSO_4$) Precipitation (Marcellus-NY sample)

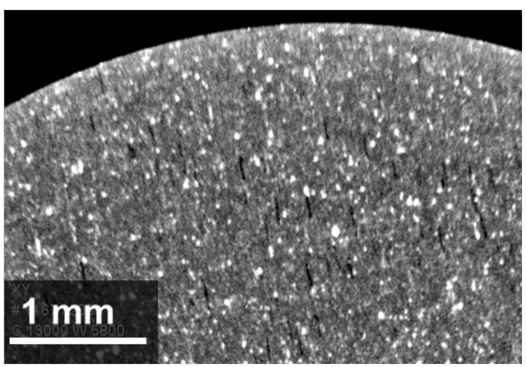
Marcellus-NY: No microcracks; Carbonate-poor

$pH_{initial}$ = 2.0; pH_{final} = 2.4-2.5

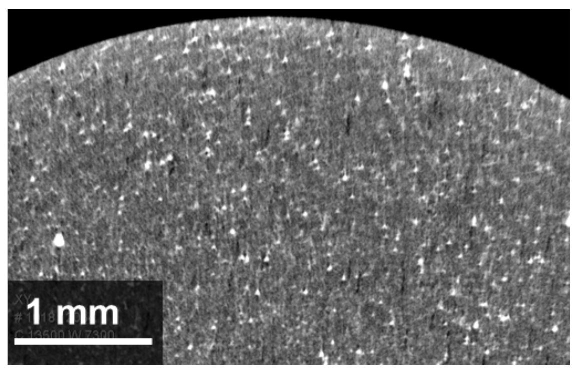
Reaction is limited due to lack of microcracks

CT slices:

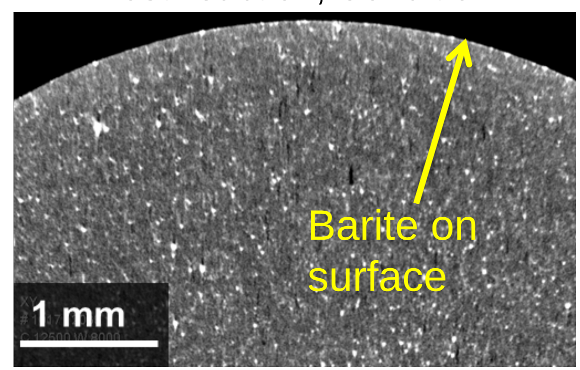
Marcellus-NY
Pre-reaction



Marcellus-NY
Post-reaction, Condition 1



Marcellus-NY
Post-reaction, Condition 2



Condition 1: FF

Condition 2: FF + 2 mM $BaCl_2$ + 0.06 mM Na_2SO_4

Barite ($BaSO_4$) Precipitation (Marcellus-PA Sample)

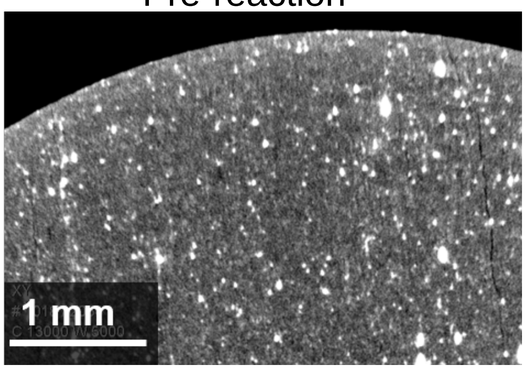
<u>*Marcellus-PA*</u>: ***Has*** microcracks; Carbonate-poor

$pH_{initial}$ = 2.0; pH_{final} = **3.6-4.0**

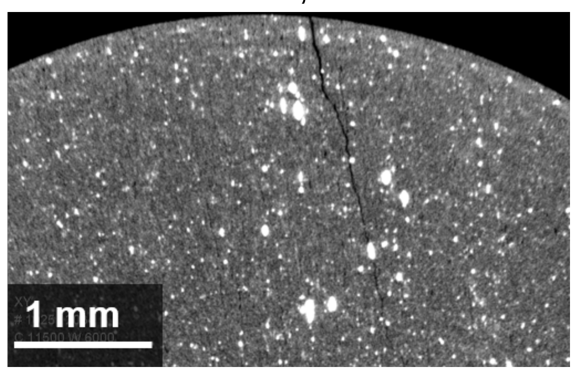
- Carbonate dissolution increased pH
- Barite precipitated on shale surface

CT slices:

Marcellus-PA
Pre-reaction

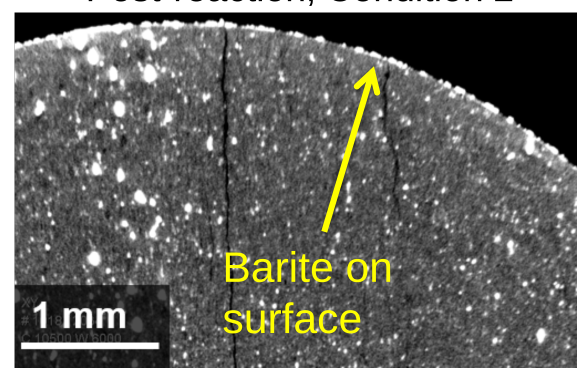


Marcellus-PA
Post-reaction, Condition 1



Condition 1: FF

Marcellus-PA
Post-reaction, Condition 2



Condition 2: FF + 2 mM $BaCl_2$ + 0.06 mM Na_2SO_4

Barite ($BaSO_4$) Precipitation (Eagle Ford Sample)

<u>*Eagle Ford*</u>: ***Has*** microcracks; **Carbonate-rich**

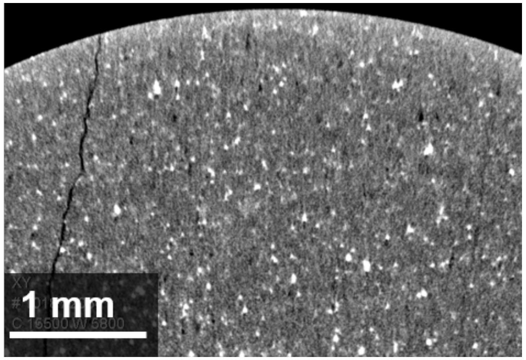
$pH_{initial}$ = 2.0; pH_{final} = **8.2**

$BaSO_4$ precipitates faster at neutral than acidic pH

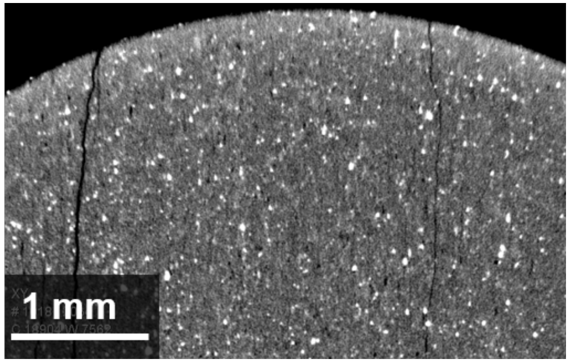
- Carbonate dissolution increased pH to neutral
- Barite precipitated in the microcracks and matrix

CT slices:

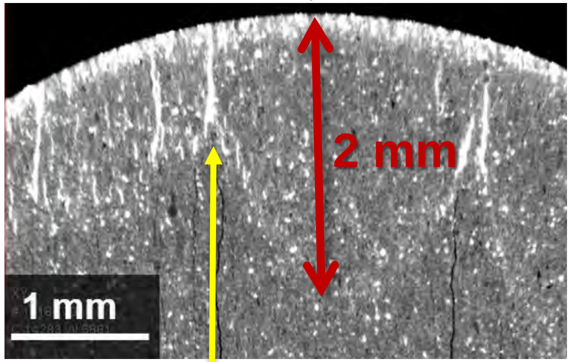
Eagle Ford
Pre-reaction



Eagle Ford
Post-reaction, Condition 1



Eagle Ford
Post-reaction, Condition 2



Barite in matrix & cracks

Condition 1: FF

Condition 2: FF + 2 mM $BaCl_2$ + 0.06 mM Na_2SO_4

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Major Conclusions

- Drilling mud appears to be the main source of Ba in unconventional systems
- Ba & SO_4 readily precipitate as pH increases
- pH buffering capacity of the shale (carbonate) controls the amount of barite scale
- Organics tested do not inhibit barite precipitation
- Microcracks promote access of acidic fluids to calcite, matrix

Ongoing work & future directions

- Basin-specific investigation of shale-fluid interactions: modeling and experiment
- Develop new fluid compositions to mitigate mineral scaling
- Use acoustic approaches to measure porosity/scale formation in-situ
- Develop new stimulation techniques/formulations to enhance shale matrix accessibility

Project Management

Accomplishments to date

- ✓ Published 6 manuscripts; 1 in press; 1 in review; 2 in preparation
- ✓ 1 Provisional Patent filed
- ✓ 19 presentations (3 invited) at national/international meetings
- ✓ Identifying major geochemical controls over barite scale precipitation and mechanisms of permeability reduction
- ✓ Demonstrated precipitation of secondary minerals and scale within shale in response to unconventional stimulation
- ✓ Modeled key fracture fluid-shale reaction networks
- ✓ Identified a new source for Ba and developed a new model on Ba-cycling in unconventional systems
- ✓ Developed model for processes controlling U release

Lessons learned

- Comparing shale-fluid reactivity across basins, compositions is critical to developing geochemical and geomechanical insights
- Coupling macroscopic and microscopic/mechanistic studies is critical
- Laboratory-based surface imaging techniques (SEM) can not be used to study reactions/precipitation occurring in shale matrix

Synergy Opportunities

COLLABORATIONS:

• Fracture-scale geochemistry	A. Hakala, C. Lopano (NETL)
• Field laboratories	MSEEL, HFTS
• Multi-length scale	LBNL (Steefel, Deng), LLNL (Morris)
• Microbial processes	S. Eisenlord (GTI), P. Mouser (OSU)
• Industrial partnerships	Pioneer (T. Spalding), Range (J. Frantz)

Project summary

Project goals: improve knowledge base - critical processes

- (i) Characterize shale alteration: nanometers to microns
- (ii) Identify geochemical controls
- (iii) Link to permeability modification
- (iv) Develop numerical models

Success criteria:

- On-time execution of PMP
- Link shale alteration to permeability
- Develop numerical models
- Presentations at national/international meetings
- Publications in major journals

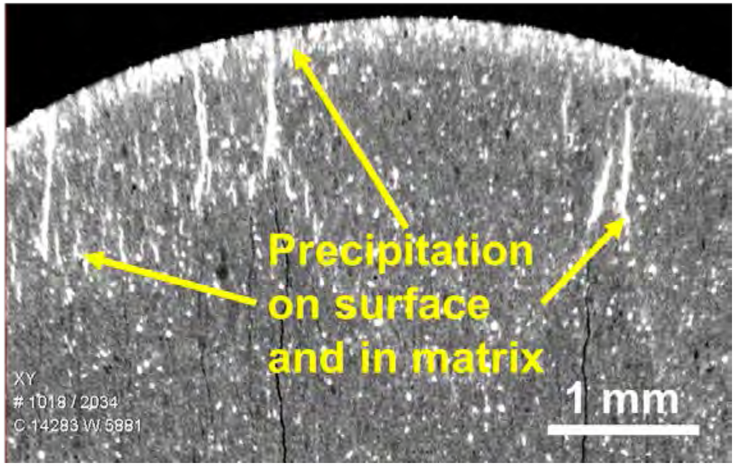
THANK YOU, NATIONAL ENERGY TECHNOLOGY LABORATORY!

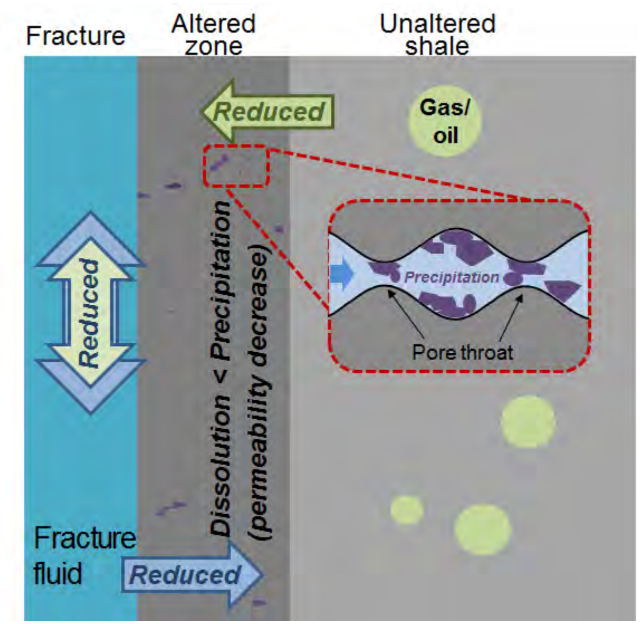
Appendices

Benefit to the Program

Program goals addressed:

- **Improve recovery factors**
- **Improve water reuse/recycling**
- **More sustainability of shale reservoirs**
- Lay foundation for **transformational advancement** of unconventional resource recovery





Fracture-fluid interfaces are crucial

Project overview

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Organization Chart, Expertise, and Roles

SLAC director
Chi-Chang Kao

SSRL director
Kelly Gaffney

Senior Scientist, Research Manager
John Bargar, Geochemistry
Synchrotron-based spectroscopy, imaging

SLAC scientific staff
Adam Jew, Research Associate
Qingyun Li, Postdoc

Co-Principle Investigators:

Stanford University

Gordon Brown, Jr., Geochemistry
Tony Kovscek, Reservoir engineering Fluid flow
Kate Maher, Geochemistry, Reactive Transport
Mark Zobak, Geomechanics

SLAC
Yijin Liu, CT Imaging

Gantt Chart – reproduced from Quarter 3 report (7-30-2018)

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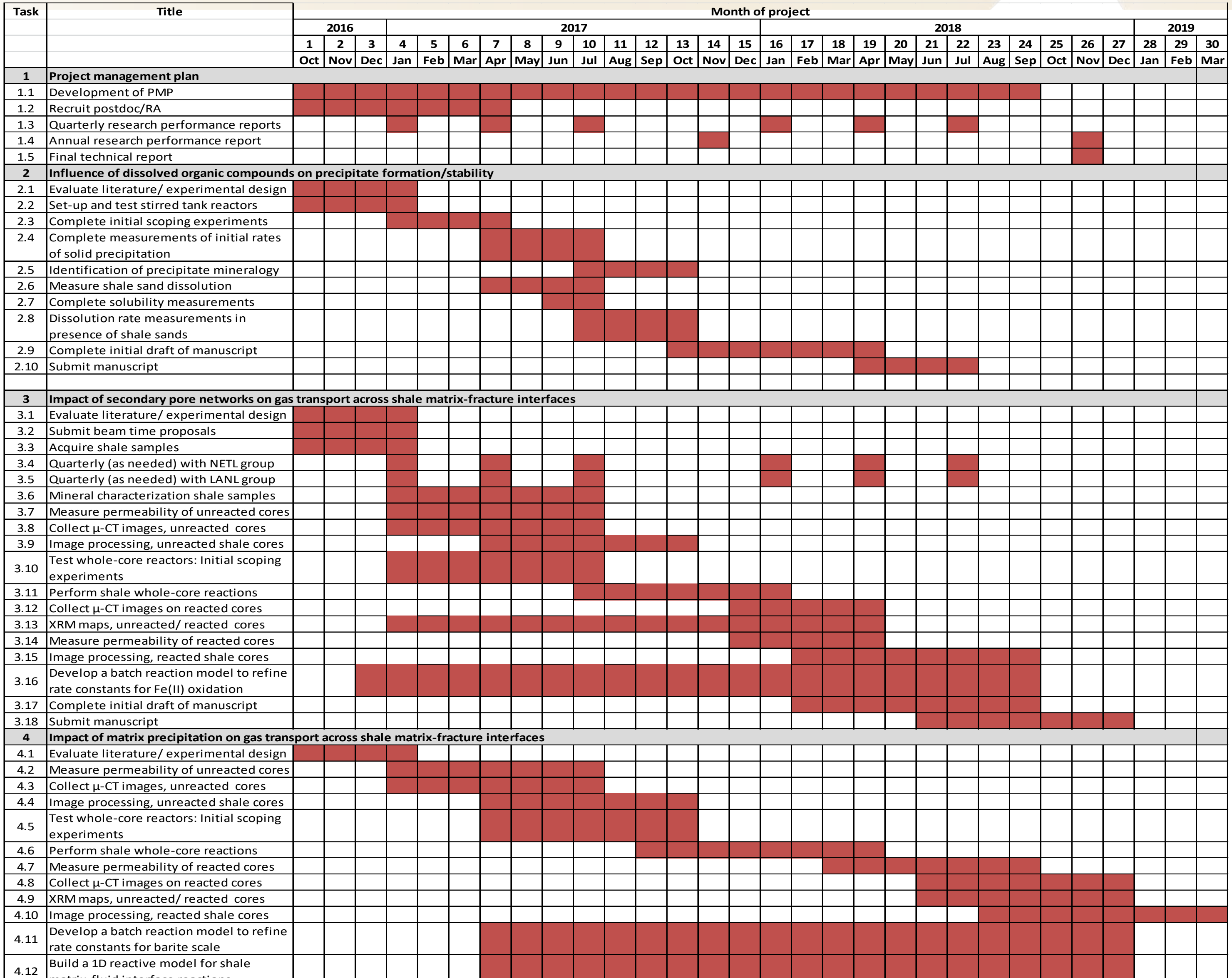

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Jew, A., Li, Q., Cercone, D., Maher, K., Brown, G. Jr., Bargar, J. 2018 Barium Sources in Hydraulic Fracturing Systems and Chemical Controls on its Release into Solution. Unconventional Resources Technology Conference Proceedings.

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Alalli, A.*, Li, Q., Jew, A., Kohli, A., Bargar, J., Zoback, M. 2018, Effects of Hydraulic Fracturing Fluid on Shale Matrix Permeability. Unconventional Resources Technology Conference.

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John R. Bargar*, Gordon E. Brown, Jr., Megan K. Dustin, Anna L. Harrison, Adam D. Jew, C.M. Joe-Wong, and Katharine Maher (2015) Geochemical control of shale fracture and matrix permeability. Shales without Scales Workshop, Santa Fe, USA, June 10. (invited)

Seminar and workshop presentations (*presenting author)

Anna L. Harrison*, Adam D. Jew, Megan K. Dustin, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) A Geochemical Framework for Evaluating Shale-Hydraulic Fracture Fluid Interactions. Stanford Center for Secure Carbon Storage Research Seminar, Stanford, USA, October 21.

John R. Bargar*, Gordon E. Brown, Jr., Megan K. Dustin, Anna L. Harrison, Adam D. Jew, C.M. Joe-Wong, and Katharine Maher (2015) Geochemical control of shale fracture and matrix permeability. Baker Hughes Incorporated, Tomball, USA, July 14. (invited)

Schematic of Ba cycling in subsurface