Geochemical Evolution of Hydraulically-Fractured Shales

NETL Research and Innovation Center
Onshore Unconventional Resources Portfolio FY16
Task 5: Water and Geochemistry

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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 16-18, 2016

Presentation Outline

- FY16 Onshore Unconventional Resources Overview
- Task 5 Overview – Program Benefits, Project Objectives and Goals
- Technical Detail: *Subsurface Geochemical Reactions*

FY16 R&IC Onshore Unconventional Resources Portfolio

- Task 1: Project management
- Task 2: Induced Seismicity and Geomechanics (Lead: Dustin Crandall)
- Task 3: Field Geophysics (Lead: Rick Hammack)
- Task 4: Air Quality (Lead: Natalie Pekney)
- Task 5: Water and Geochemistry (Lead: Alexandra Hakala)

Benefit to the Program

- Facilitating a safe and environmentally sustainable supply of natural gas
  - Efficient resource development and associated footprint reduction
  - Subsurface science in the context of understanding the reservoir
  - Water quality and availability

- Research projects within *Task 5: Water and Geochemistry* will result in the following benefits:
  - Improved understanding of hydraulically-fractured reservoirs:
    - Characterize fluid-shale reactions that affect the reservoir and produced water composition
    - Identify microbiological populations present in hydraulically-fractured shales that can affect reservoir processes and well integrity
  - Ensuring protection of surface waters and shallow groundwaters (Water Quality):
    - Evaluate changes to well cement integrity in the presence of reactive geologic fluids and methods for monitoring well integrity
    - Identify best practices for waste disposal to minimize environmental impact

Project Overview:
Goals and Objectives
Task 5: Water and Geochemistry

1. Understand effects of biological and chemical processes on unconventional oil and gas reservoir performance.
2. Develop tools for detection of chemical changes in the hydrocarbon reservoir and shallow receptors of released fluids and gas.

Surface System Responses

Identify best practices for waste disposal to minimize environmental impact

Gas Well Cement Integrity

Evaluate changes to well cement integrity in the presence of reactive geologic fluids

Subsurface Geochemical Reactions

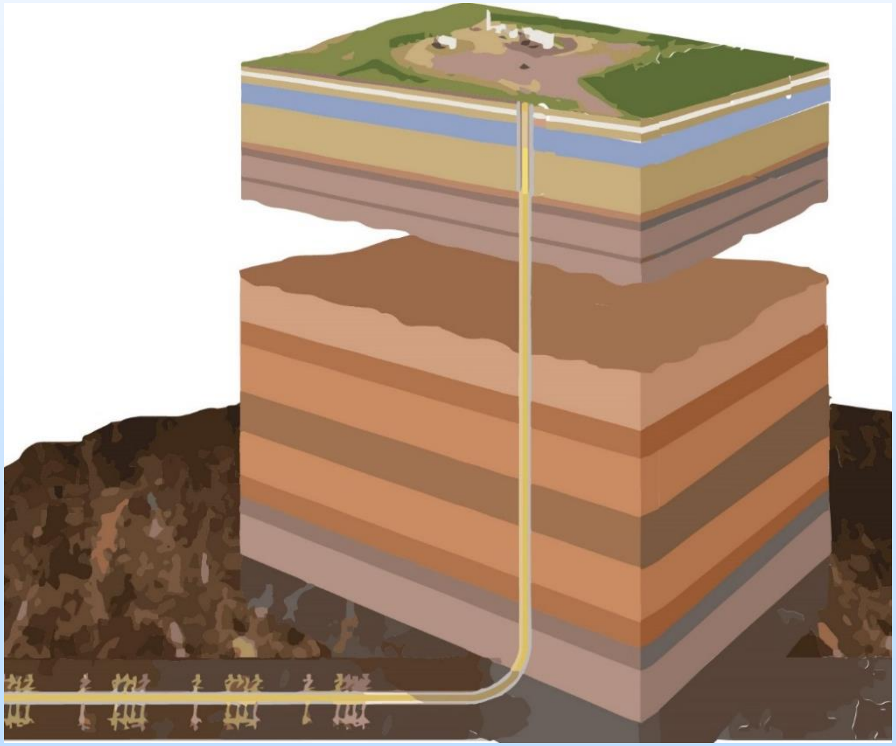
Characterize fluid-shale reactions that affect the reservoir and produced water composition

Microbial Communities and Biocides

Identify microbiological populations and biocide reactions in fractured shales

Sensors for In Situ Measurements

Develop sensors for monitoring well integrity



How do we characterize and monitor the mineral reactions that could affect flow in fractured shales?

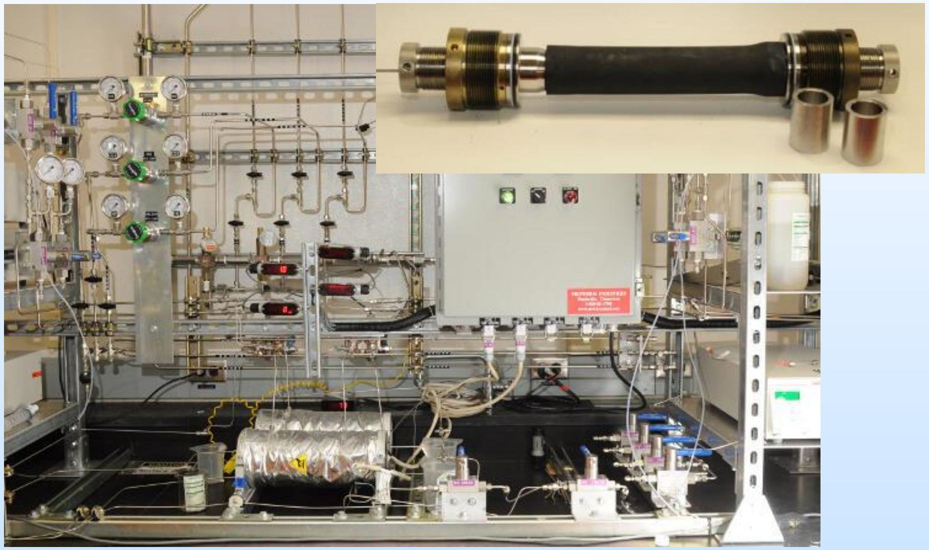
- Evaluate the shut-in period
- Compare chemical changes in the presence and absence of fracturing chemicals
  - Mineral Reactions – *could these affect flow?*
  - Changes in Fluid Chemistry – *what needs to be monitored for water treatment design, and to tell us what's happening downhole?*
- ***Apply NETL's experimental and analytical geochemistry capabilities to evaluate how fracturing chemicals react with shale***

Mineral reactions and organic geochemical changes observed in lab-scale experiments

- Mineral reactions observed and modeled:
  - Calcite dissolution
  - Barite, gypsum, anhydrite, secondary smectite and carbonate precipitation
- Trace metal chemistry is controlled by secondary mineral precipitation
- Shale reactions with frac fluids result in changes to fluid and solid phase organic chemistry
- Geochemical tracers provide excellent signals for differences between formations
  - Ability to track fracture-scale reactions may be limited

Application of NETL R&IC's experimental and analytical geochemistry capabilities to evaluate frac chemical-shale reactions

High-pressure, high-temperature Static and Flow-through reactor systems (Geological and Environmental Systems Directorate, GES)



Analytical geochemistry & geochemical modeling (GES) and characterization (Materials Engineering and Manufacturing Directorate, MEMD)

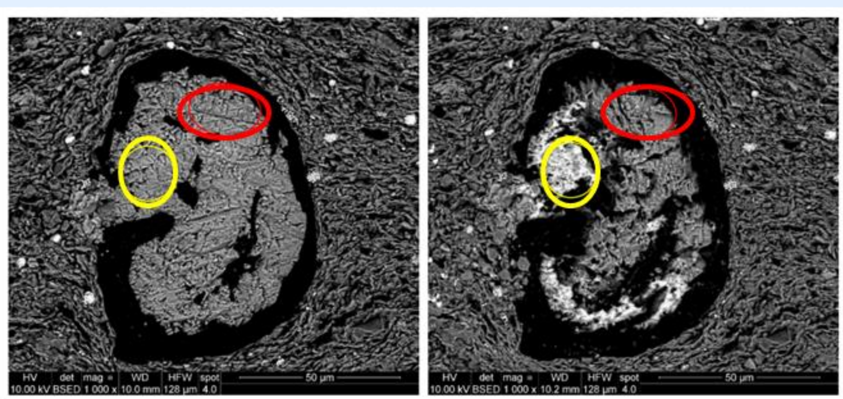
- Metal isotopes: Multicollector ICP-MS
- Organic geochemistry: LC-QTOF-MS, IC, GC-MS
- Visualization: environmental SEM, CT scanning

Static autoclave experiments to evaluate changes in shale after exposure to high-TDS frac fluids – 1 of 2

Static autoclave, polished Marcellus Shale before and after exposure to synthetic high-TDS fluid. Reacted at 77°C and 4000 psi for 6 days.

Post-exposure gypsum precipitation, calcite dissolution

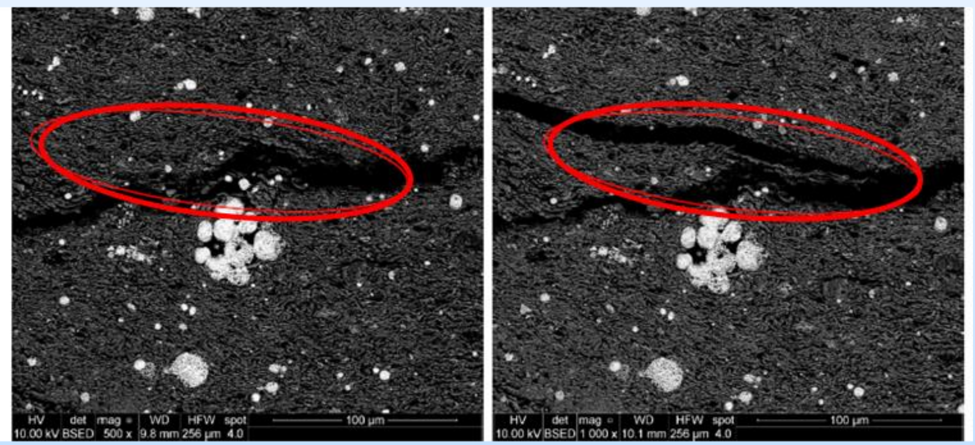
Pre-exposure | Post-exposure



1000x magnification

Post-exposure fracture growth

Pre-exposure | Post-exposure



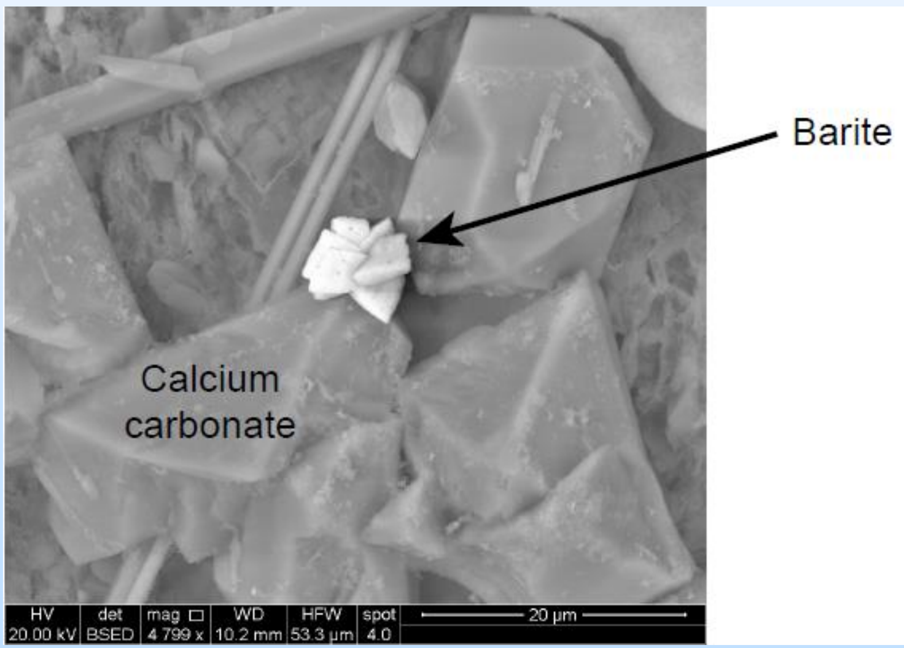
500x magnification

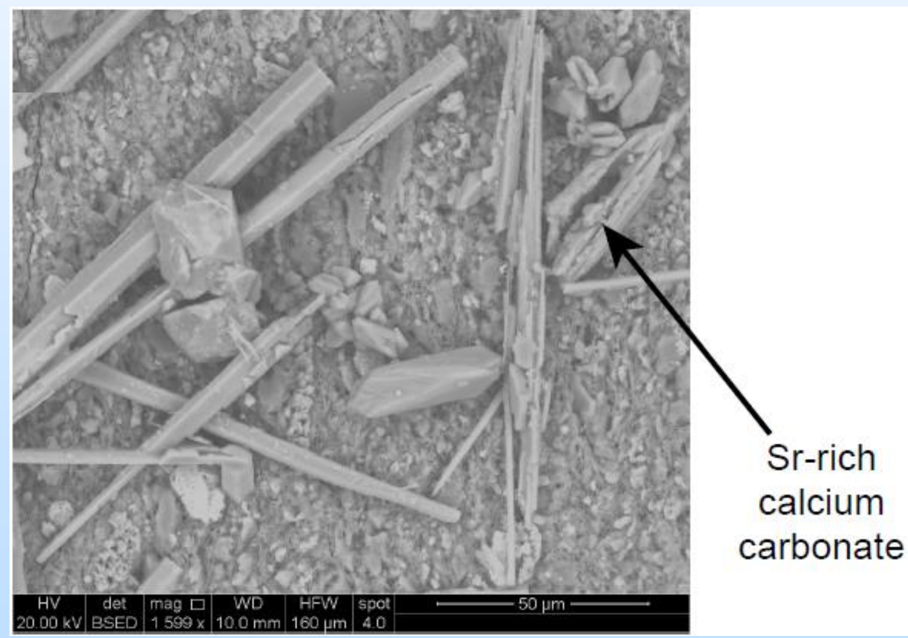
Dieterich, Kutchko, and Goodman (2016) *Fuel*

Static autoclave experiments to evaluate changes in shale after exposure to high-TDS frac fluids – 2 of 2

Static autoclave, polished Marcellus Shale after exposure to synthetic high-TDS fluid.
Reacted at 85°C and 4000 psi for 5 days.

Barite and Sr-rich calcium carbonate observed on reacted shale surfaces





Mineral reactions and organic geochemical changes observed in lab-scale experiments

- Mineral reactions observed:
  - Calcite dissolution
  - Barite, gypsum, and carbonate precipitation

Experiment 1:
High-TDS Fluid + Shale

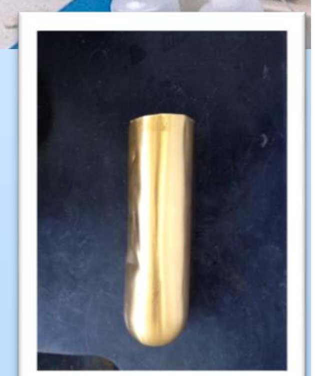
Fluid: 100% Synthetic Brine

Solid: Marcellus shale chips and powder (Greene County)

Water to Rock Ratio: 20.4 to 1

pH_0: 7.59 ± 0.1

15 d, 130°C, 4000 psi



Analytical & Modeling Tools:

- ICP-OES, ICP-MS, IC, LC-QTOF, GC-MS
- Coulometry, SEM, XRD
- GWB for modeling

Experiment 2:
High-TDS Fluid + Shale + Fracturing Chemicals

Fluid: 70% Synthetic Brine, 30% Fracturing Fluid

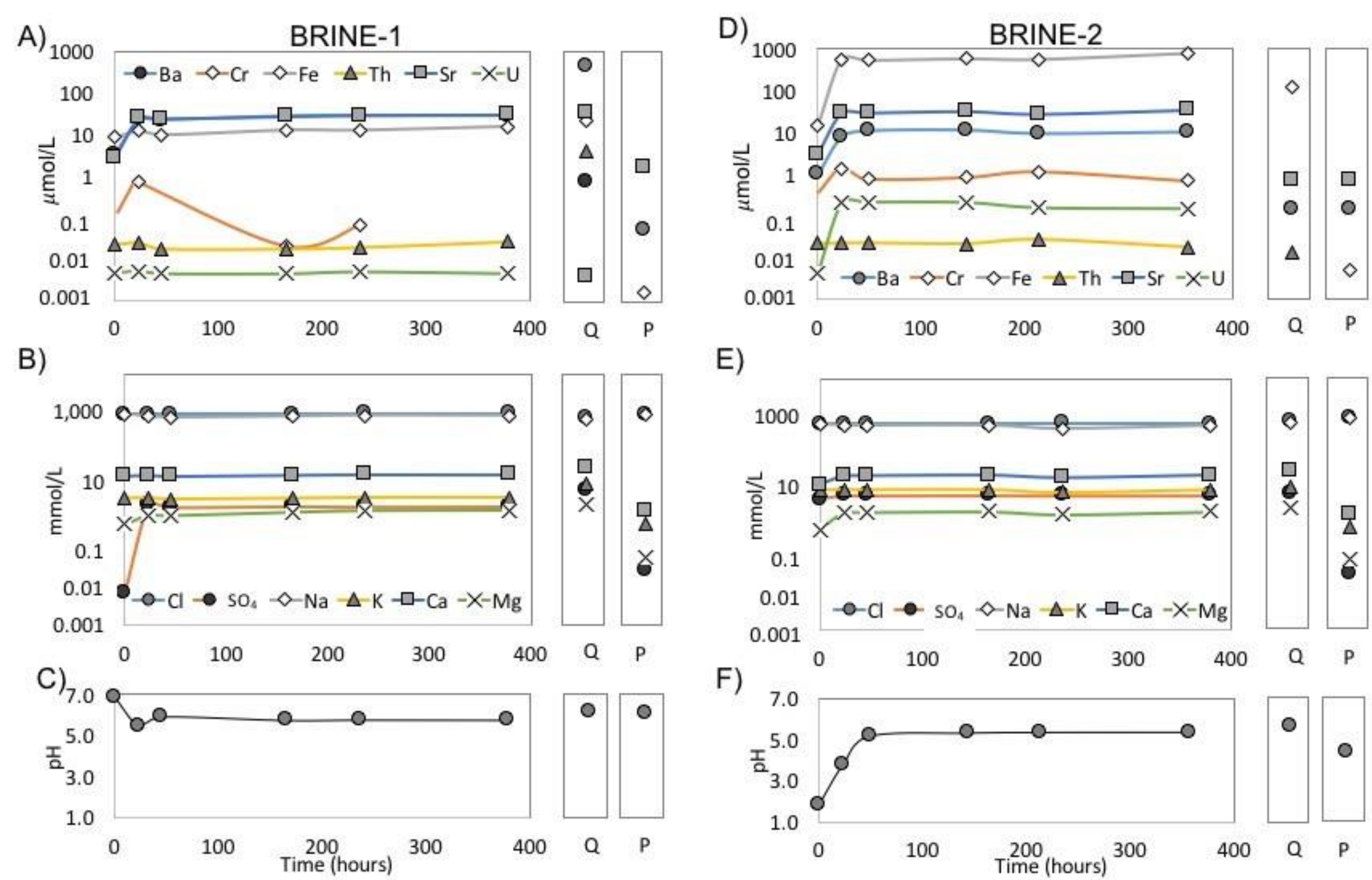
Solid: Marcellus shale chips and powder (Greene County)

Water to Rock Ratio: 18.6 to 1

pH_0: 1.83 ± 0.1

Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry

Most solution chemistry changes occur within 48 hours of bringing the experiment to elevated P,T

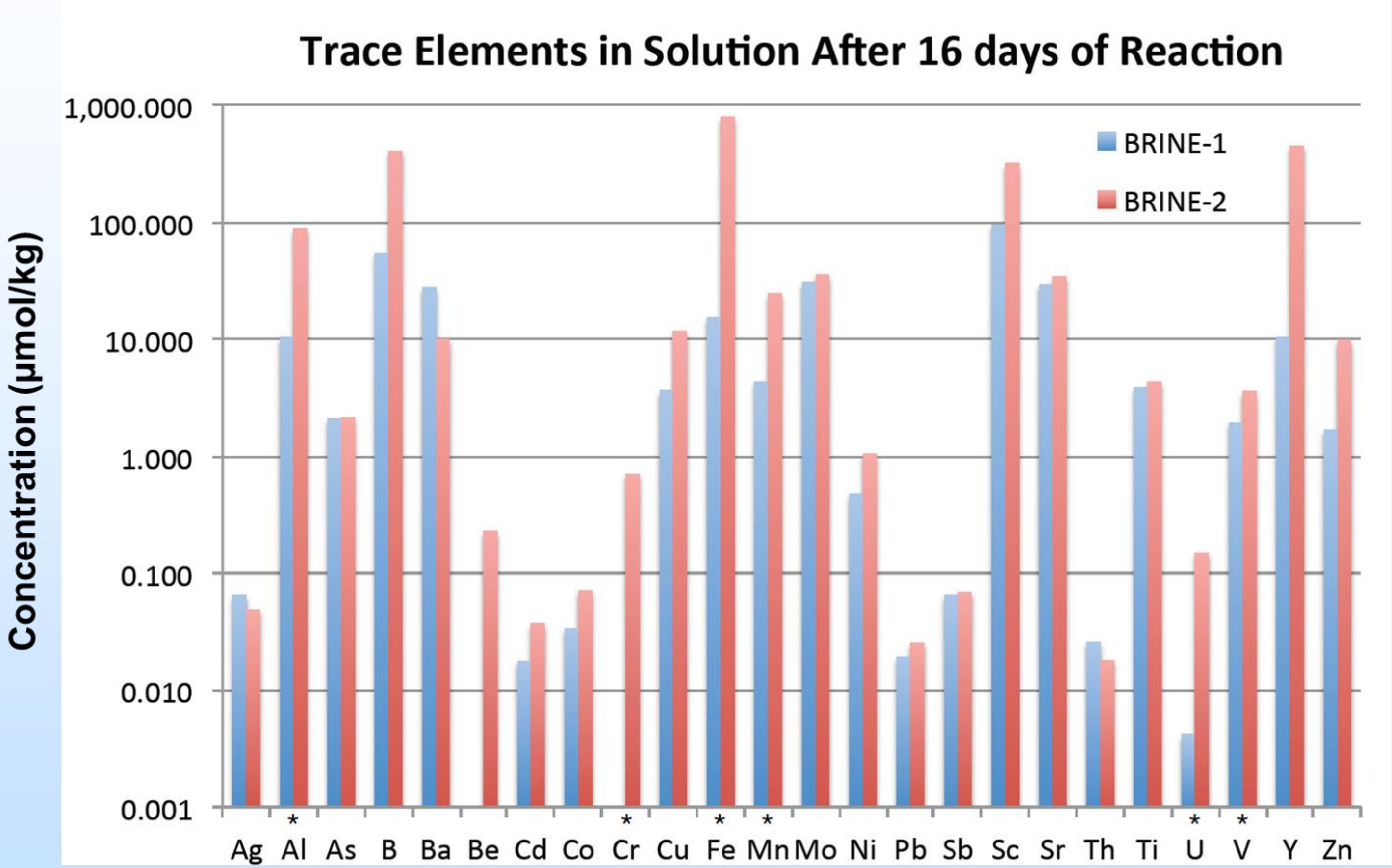


Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry

Most elements show elevated concentrations in the experiment with fracturing chemicals after 16 d

Elements enriched *in presence of* fracturing fluids:
Al*, As, B, Be, Cd, Co, Cr*, Cu, Fe*, Mn*, No, Ni, Pb, Sb, Sc, Sr, Ti, U*, V*, Y, Zn
K*, Ca*, Mg*

Elements enriched *in absence of* fracturing fluids:
Ag, Ba, Th



* Denotes statistically significant enrichment based on Pearson correlation coefficients

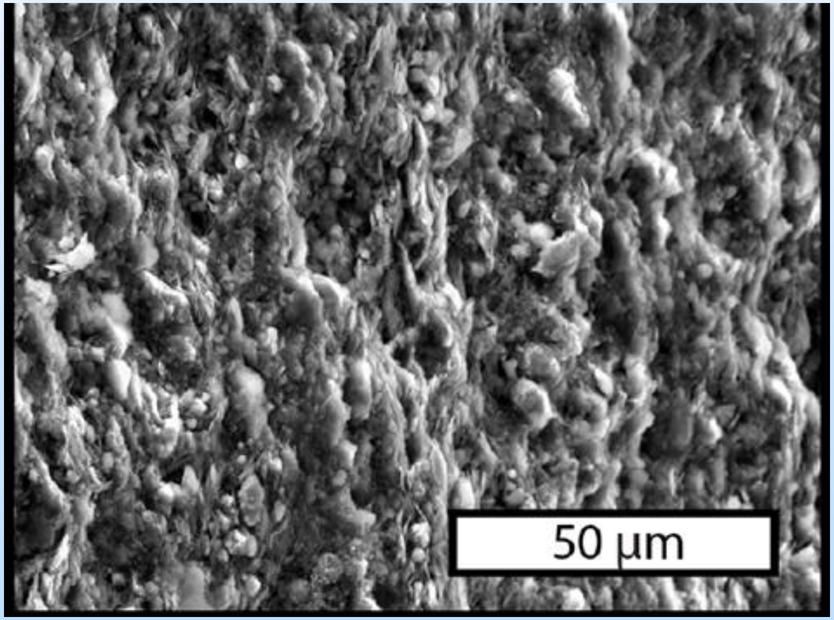
Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry

Evidence for significant carbonate dissolution in experiments containing fracturing fluids

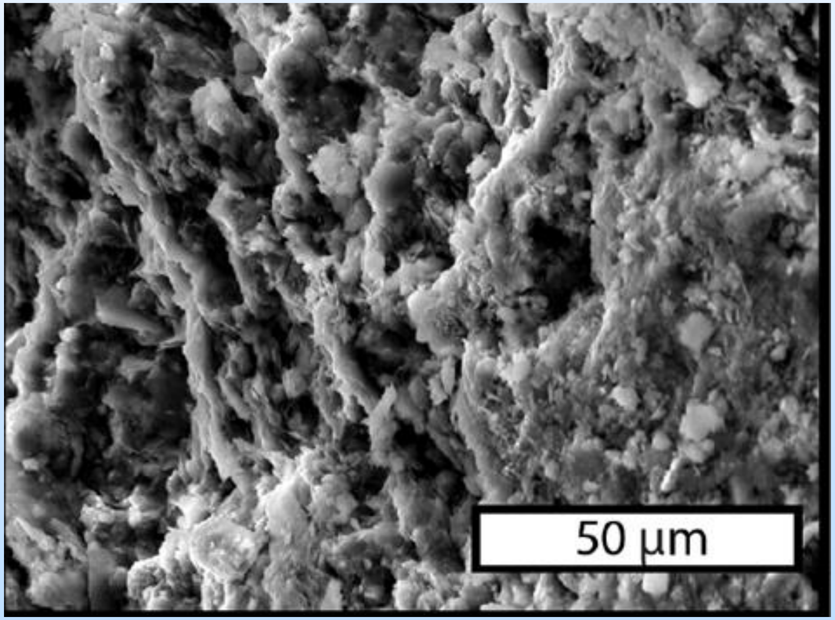
Inorganic Carbon (% carbon)	
Unreacted	0.528 ± 0.002
Brine +Shale	0.457 ± 0.002
Brine+Shale+Frac Fluid	0.208 ± 0.004

Supported by XRD patterns

Brine + Shale



Brine + Shale +Frac Fluid



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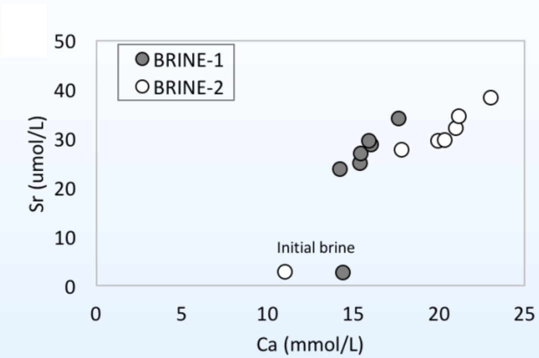
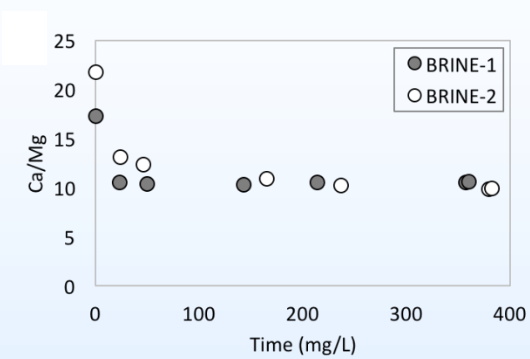
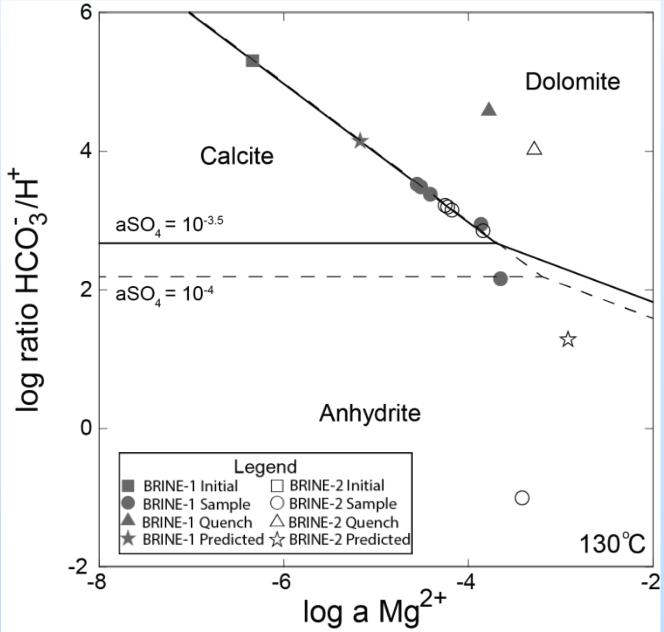
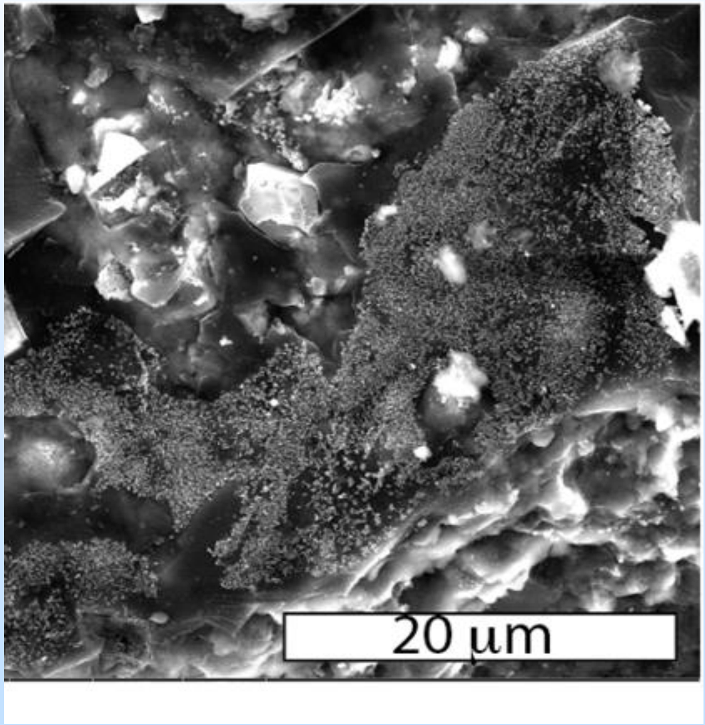
Evidence for secondary precipitation of carbonates and anhydrite



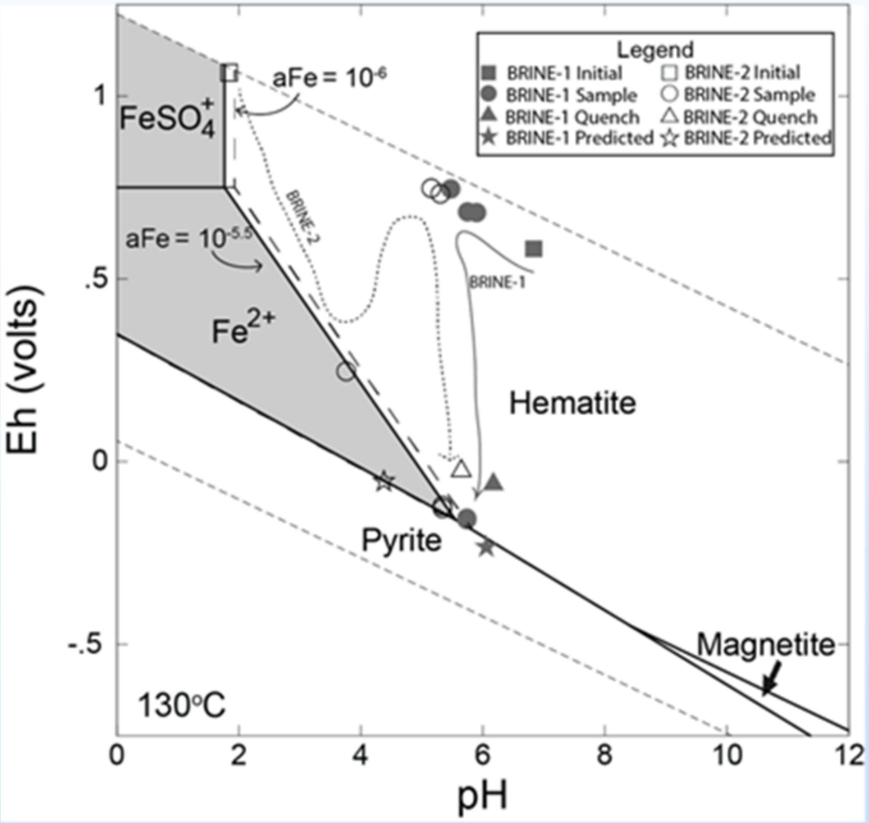


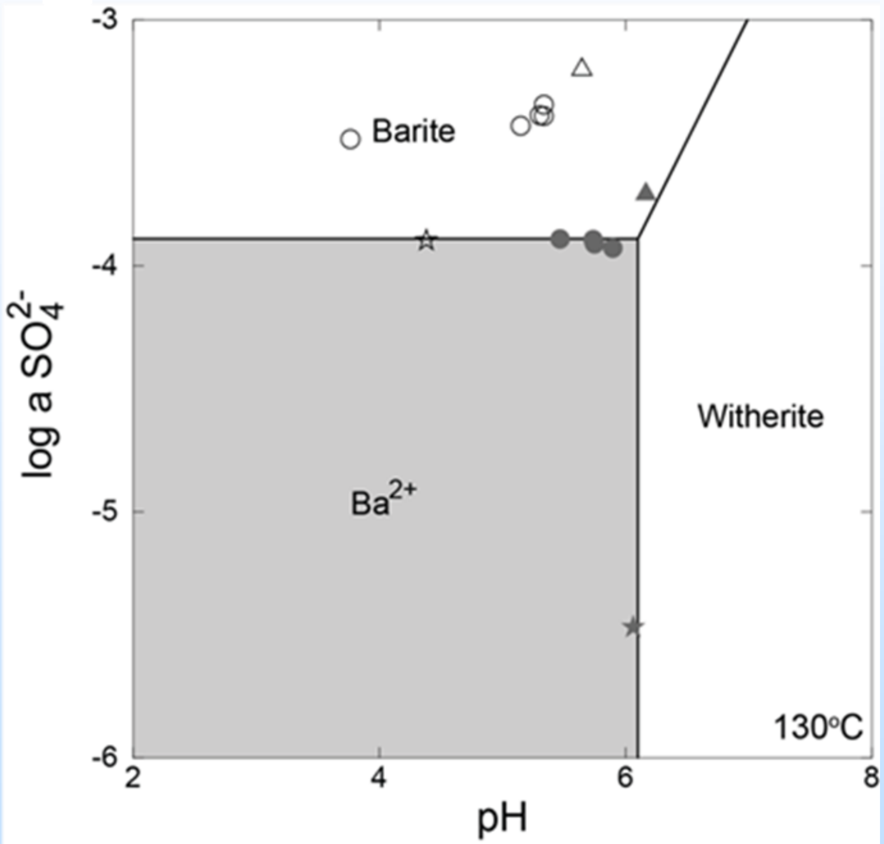




Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry

Redox changes, and may influence barite stability as observed by modeling fluid chemistry

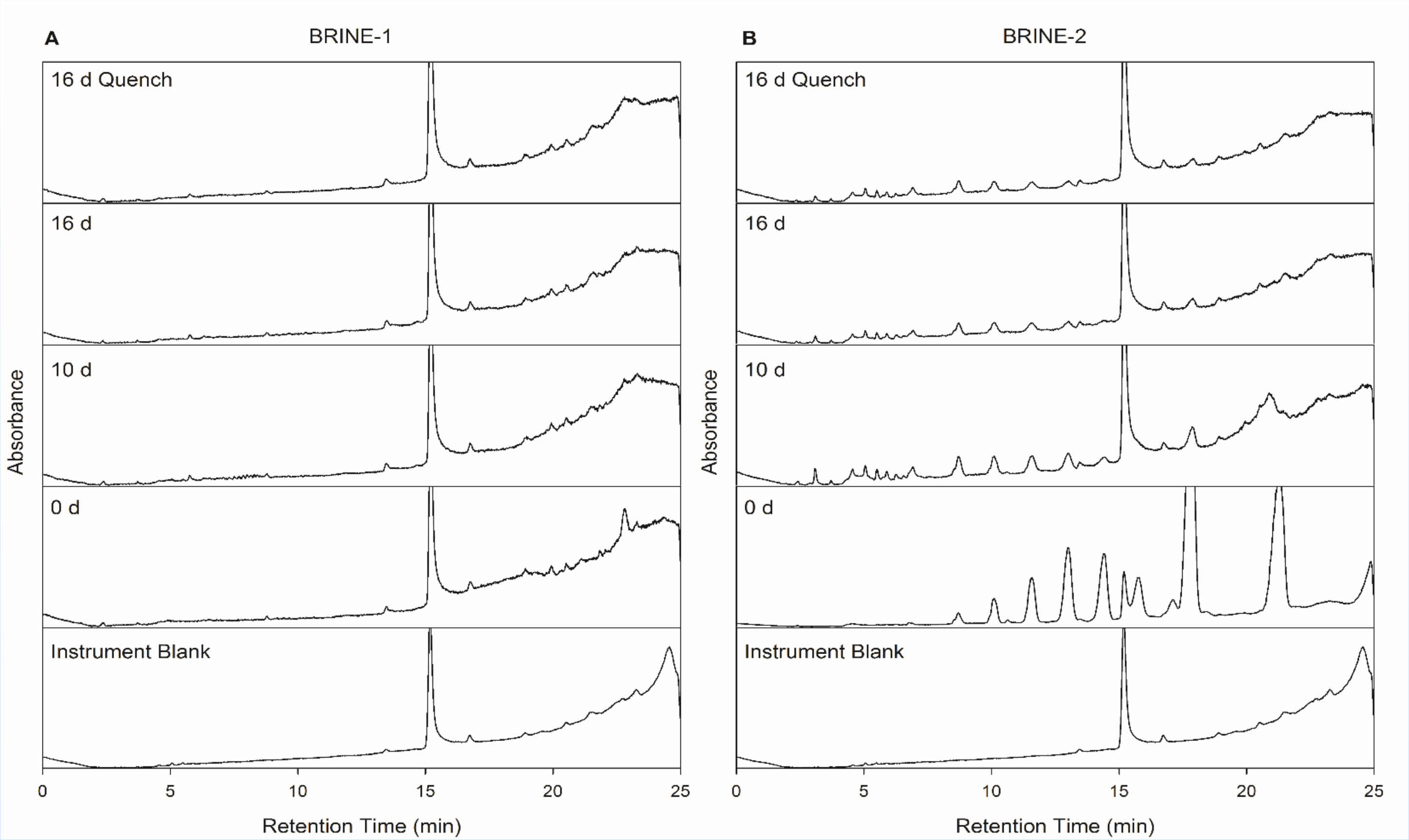




Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry

Changes in aqueous organic composition observed for the experiment containing frac fluids: LC-QTOF

Rocking autoclave, Marcellus Shale chips + powder, 15 d, 130°C, 4000 psi
BRINE-1: synthetic brine, BRINE-2: Fracturing fluid + synthetic brine



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Changes in aqueous organic composition observed for the experiment containing frac fluids: GC-MS

Rocking autoclave, Marcellus Shale chips + powder, Fracturing fluid + synthetic brine, 15 d, 130°C, 4000 psi

	Time (days)			
Reacted Samples	**0**	**9.8**	**16.3**	**Observations**
1-Octanol	X			
2-Butoxyethanol	X	X	X	Slight decrease in the abundance from 0 to 16.3 days
4-Ethoxybenzoic Acid Ethyl Ester	X	X	X	Decreased from 0 to 16.3 days sample
Acetic Acid		X		
Benzene			X	
Dimethylbenzene		X	X	Increased abundance from 9.8 to 16.3 days
Fural or 3-Furaldehyde		X	X	Only observed in later samples
N,N-dimethyl-1-dodecanamine	X			
Napthalene	X	X	X	Present in all samples
Nonanol		X		
Tetrahydronaphthalene	X	X	X	Present in all samples
Toluene			X	
Trimethylbenzene		X	X	Increase in Benzene from 9.8 to 16.3 days

Marcon, Joseph, Carter, Hedges, Lopano, Guthrie, Hakala, Under Review, Applied Geochemistry

Mineral reactions and organic geochemical changes observed in lab-scale experiments

- Mineral reactions observed and modeled:
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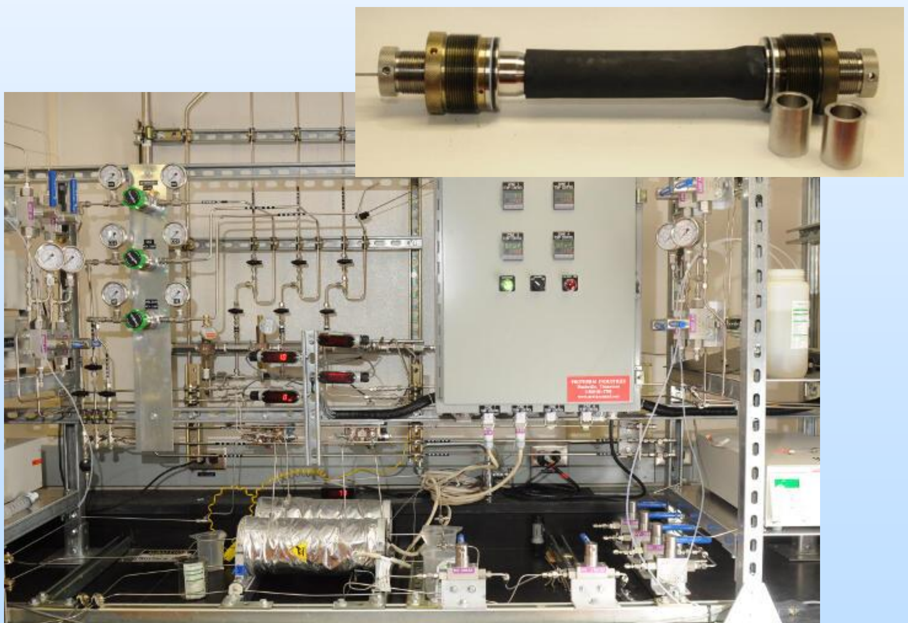
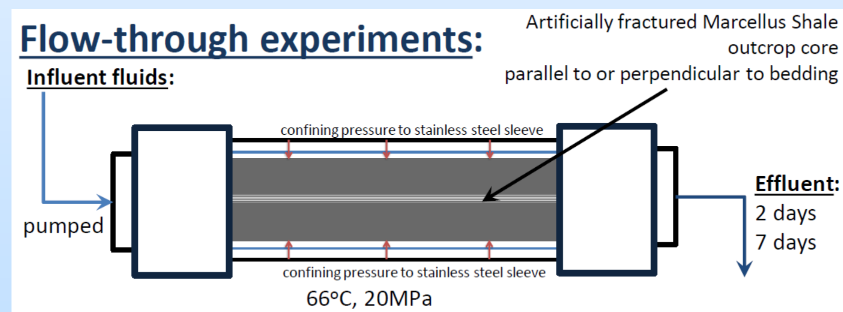
- Trace metal chemistry is controlled by secondary mineral precipitation
- Shale reactions with frac fluids result in changes to fluid and solid phase organic chemistry

Flow-through experiments to evaluate effects of flow on mineral dissolution and precipitation

- Are observations from static and rocking autoclave experiments consistent with a system under flow?
- Can geochemical tracers (metal isotopes) provide insight on mineral dissolution and precipitation?

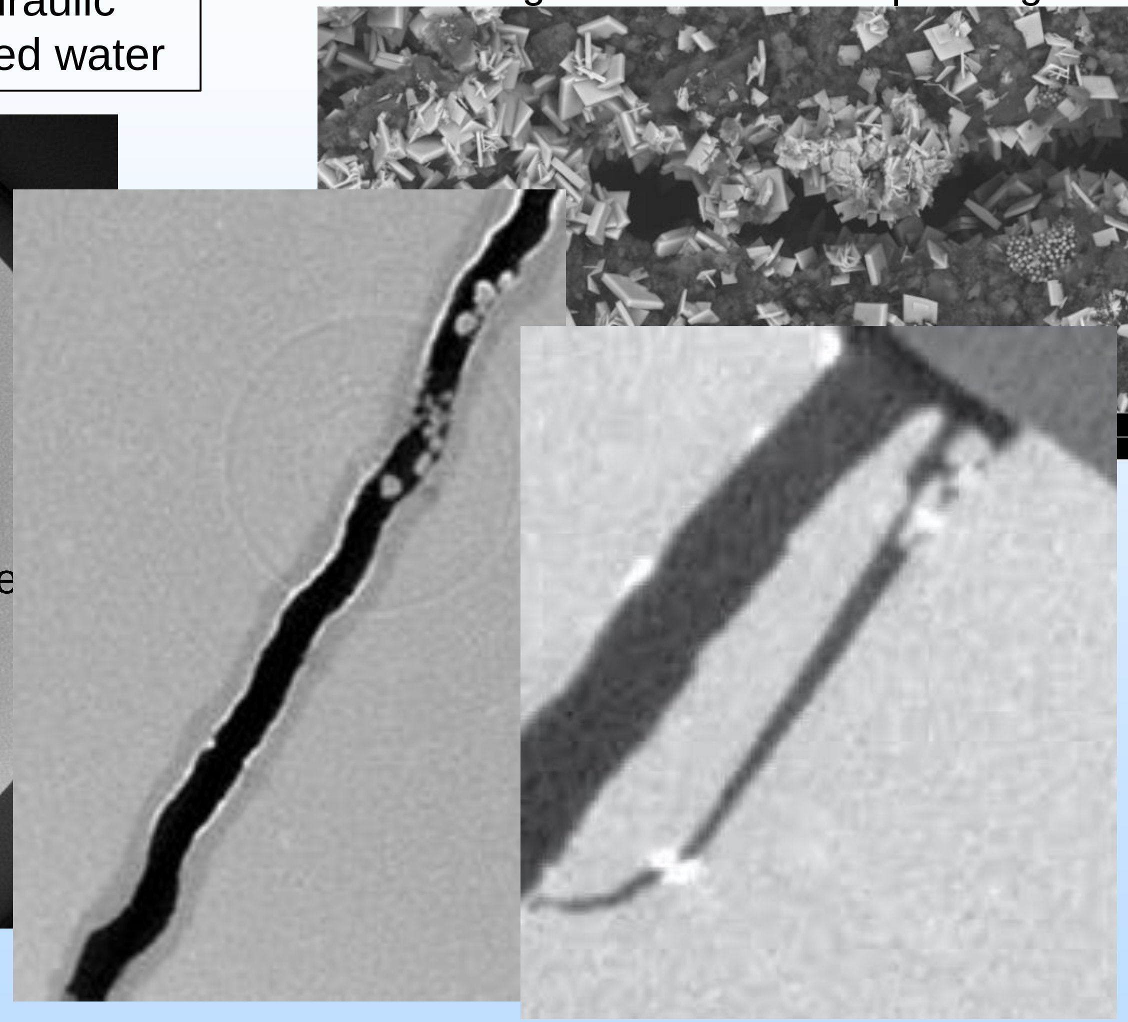


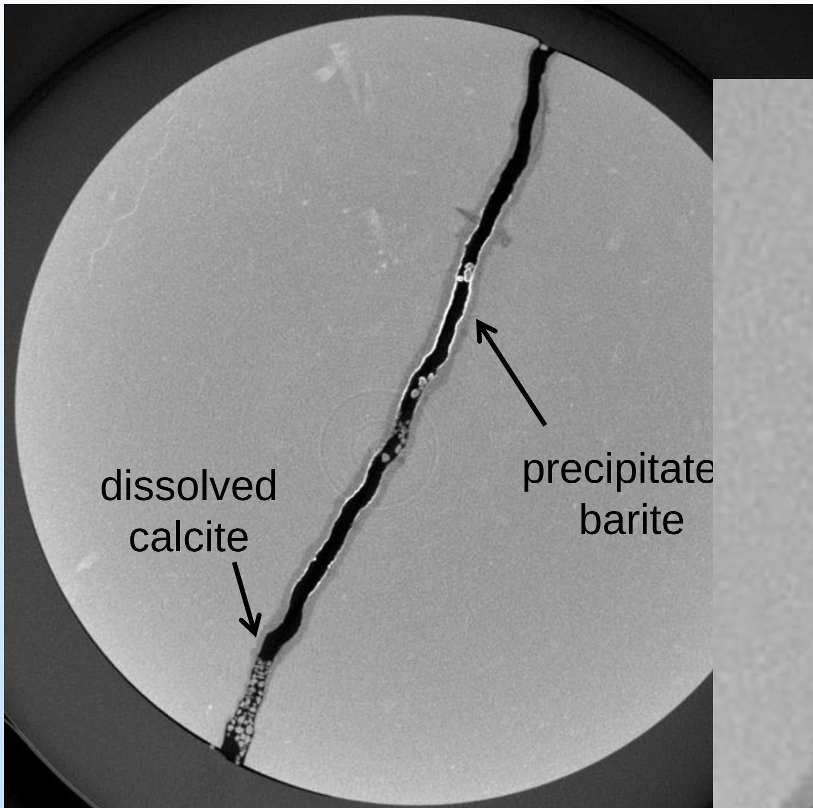


Barite formation observed in flow-through experiment containing reused produced water + frac chemicals

Marcellus shale reacted with hydraulic fracturing fluid from reused produced water

Scanning electron microscope image



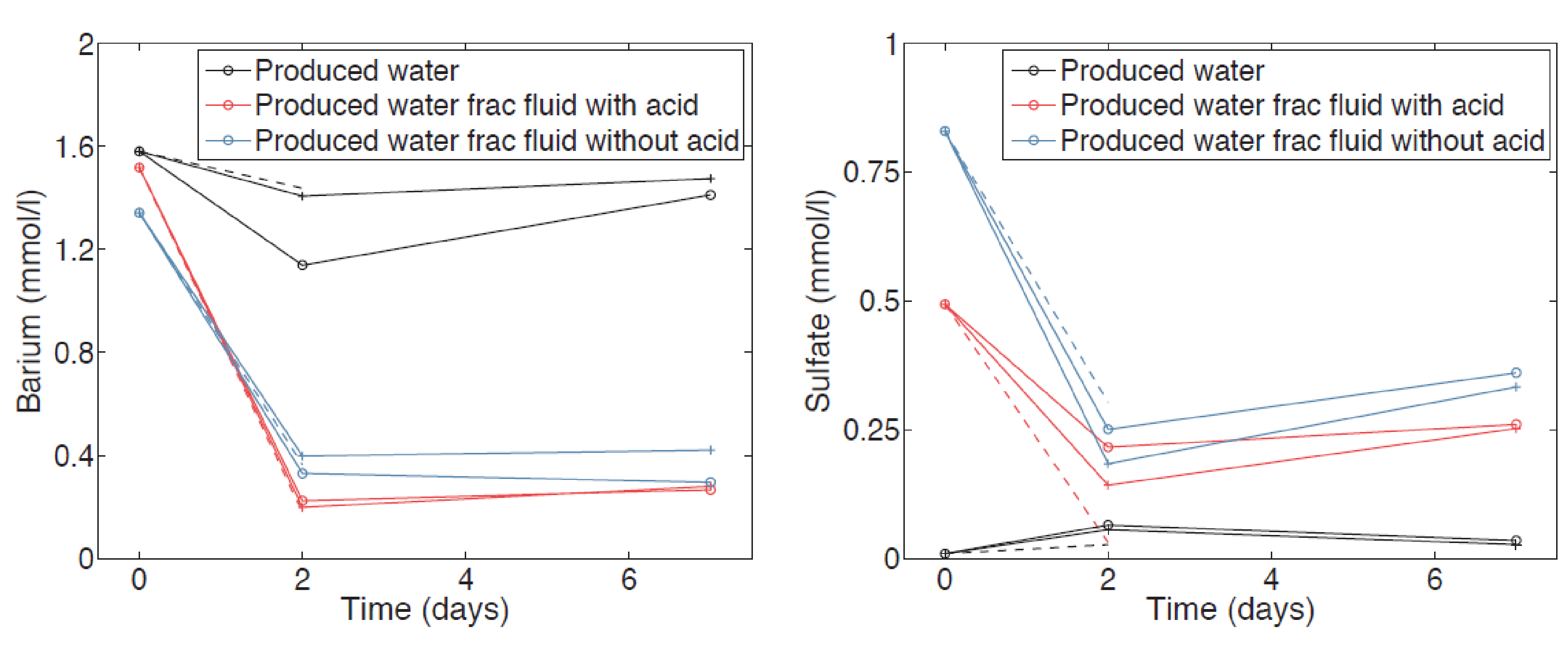


X-ray computed tomography image

Paukert, Hakala, Jarvis, AGU Fall Meeting, December 2015; in preparation

Fluid chemistry for flow-through control experiment also shows Ba and SO_4^{2-} decrease

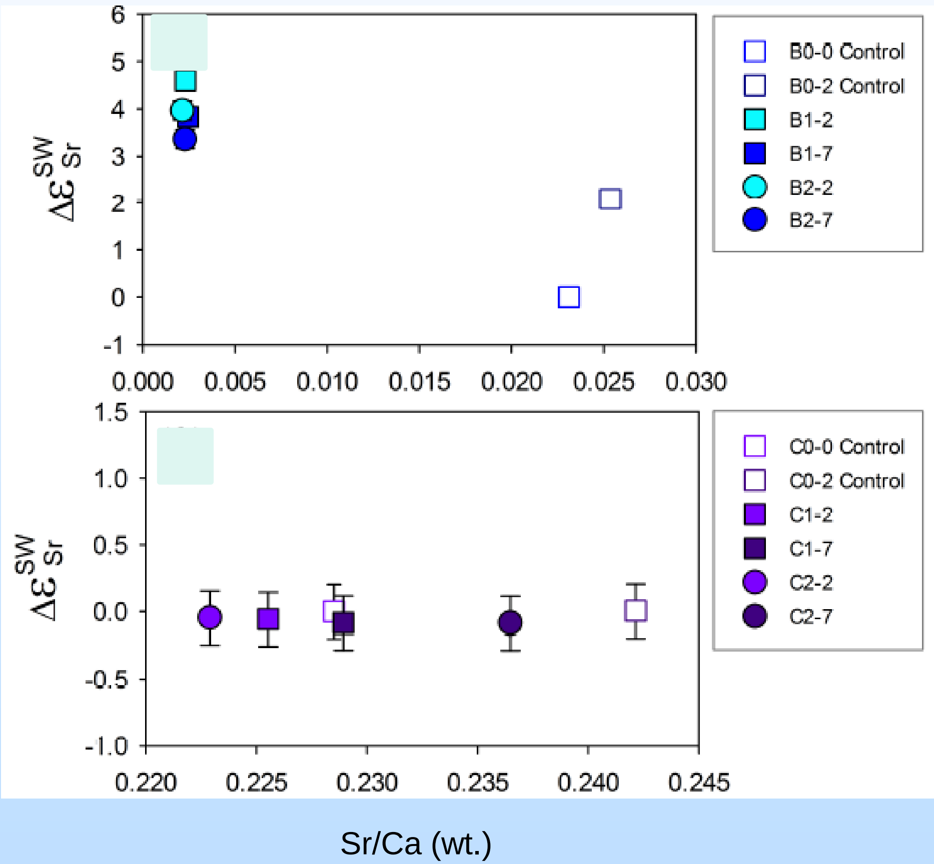
Implication: Scale inhibitor may not be performing as expected

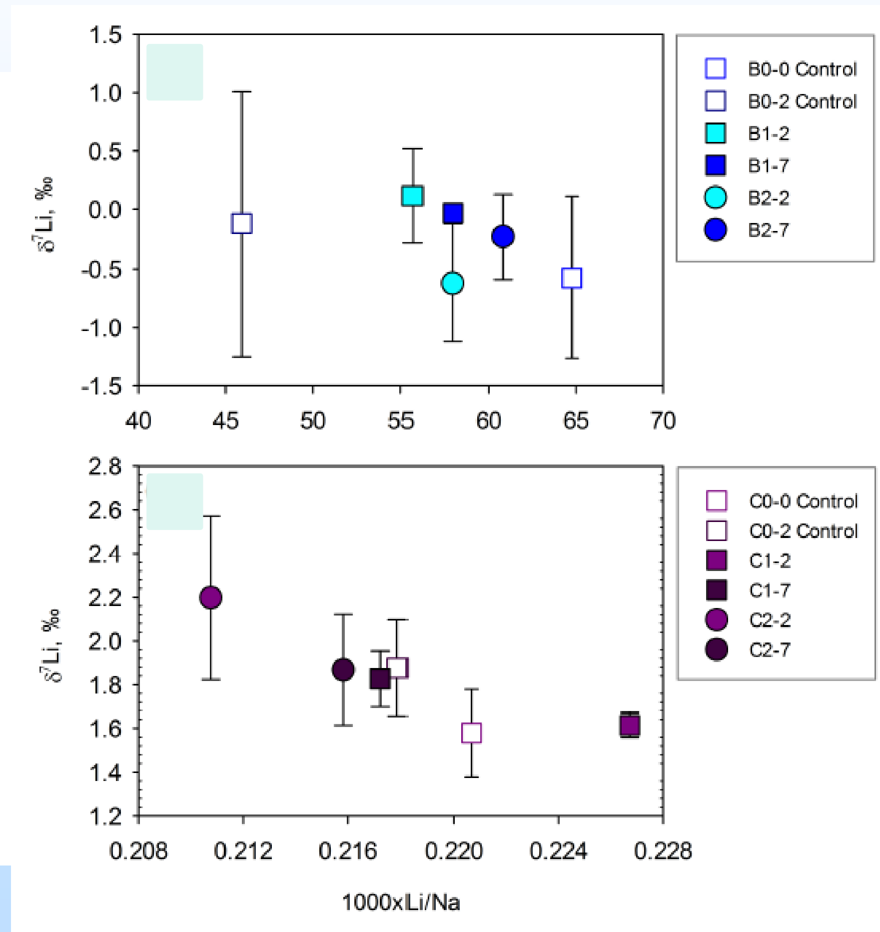


Paukert, Hakala, Jarvis, AGU Fall Meeting, December 2015; in preparation

Minimal changes in Sr and Li isotope signatures observed for shale-frac fluid reactions

Implication: Although useful for monitoring basin-scale fluid mixing, Sr and Li isotopes show limited application as indicators for frac fluid shale interactions





Phan, Paukert, Hakala, AGU Fall Meeting, December 2015; in preparation

Mineral reactions and organic geochemical changes observed in lab-scale experiments

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- Trace metal chemistry is controlled by secondary mineral precipitation
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- Geochemical tracers provide excellent signals for differences between formations
  - Ability to track fracture-scale reactions may be limited

Accomplishments to Date
Onshore UCR Task 5: Water and Geochemistry

Time Period	Accomplishments
Historical - FY 15	• Batch experiments showed that fracturing fluids affect shale mineral reactions through pH and redox based reactions • Fiber optic-based pH sensing applications developed for aqueous subsurface environments • Air drilling identified as a plausible cause for groundwater methane transport as shown through 3D TOUGH 2 modeling
Current - FY 16	• Fracturing fluid-shale mineral reactions observed to result in mineral dissolution and precipitation along fractures, however have a limited influence on produced water total dissolved solids • Completion of largest microbial characterization survey of hydraulically-fractured environments to date • Gas well cement mineralogy and structures are affected by coal mine water • Leaching of metals and salts from drill cuttings disposal sites can vary by drilling method, elements of interest, and disposal site geochemical conditions • New approaches were developed for surface water monitoring of produced water spills, and shallow groundwater monitoring of methane migration • Dissolved iron and pyrite influence the degradation rate of biocides introduced to shale formations during hydraulic fracturing
Future - FY 17	• Focus on water systems, continue with leaching studies and modeling; monitoring and geochemical analysis approaches • Add produced water treatment and planning, geospatial approach to establishing base of groundwater

Synergy Opportunities

- Pore to Core Scale Processes in Shale
  - NETL, LANL, SSRL, LBNL, Sandia Collaborations – Meeting on July 14, 2016
  - Leveraging research across multiple portfolios (unconventional oil and gas resources; geologic CO_2 storage)
  - Focus on shales
- Coordinate experimental efforts with SSRL with a focus on organic geochemical reactions and barite geochemistry
- Other opportunities to-be-identified

Summary

- Next steps for hydraulically-fractured reservoir shale geochemistry
  - Evaluate secondary mineral precipitation along a fracture flow pathway – can precipitation benefit fracture propping?
  - Cement reactions involving the near-wellbore environment?
  - More in-depth investigation related to organic geochemistry and microbiology of these systems

Appendix

Organization Chart

- Describe project team, organization, and participants.
  - Link organizations, if more than one, to general project efforts (i.e. materials development, pilot unit operation, management, cost analysis, etc.).
- Please limit company specific information to that relevant to achieving project goals and objectives.

Organization Chart: R&IC Onshore UCR

	FY 2016	FY 2017 and Future
Technical Portfolio Lead (TPL)	No TPL; Portfolio coordinated by TTCs	Alexandra Hakala
Team Technical Coordinators (TTC)	Task 1: Project Management – Alexandra Hakala Task 2: Induced Seismicity and Geomechanics – Dustin Crandall Task 3: Field Geophysics – Rick Hammack Task 4; Air Quality – Natalie Pekney Task 5: Water and Geochemistry – Alexandra Hakala	Task 1: Project Management – Alexandra Hakala Task 2: Reservoir Processes – Dustin Crandall Task 3: Wellbore Issues – Barbara Kutchko Task 4: Seismicity Issues – Rick Hammack Task 5: Water Issues – Alexandra Hakala Task 6: Air Quality Issues – Natalie Pekney Task 7: Hybrid Energy Systems – Mark McKoy Task 8: Systems Analysis for Onshore UCR – Donald Remson

Organization Chart: R&IC Onshore UCR
Water and Geochemistry Projects, 1 of 2

FY 2016

Task 5: Water and Geochemistry, TTC: Alexandra Hakala

Project	Principal Investigator	Team Members (NETL, ORISE, AECOM)	External Partners
Fluid and Solid Isotope Characterization at MSEEL	Alexandra Hakala	Thai Phan, Christina Lopano, Tracy Bank, Bill Garber	Shikha Sharma (WVU), Brian Stewart (Pitt)
Characterize chemistry of drill cuttings leachates	Christina Lopano	Mengling Stuckman, Alexandra Hakala	
Comparison of microbial ecology in fractured shales	Djuna Gulliver	Daniel Lipus	Kyle Bibbey (Pitt)
Biocide effectiveness through reactivity with shale minerals	Alexandra Hakala	Jinesh Jain	Athanasios Karamalidis, Nizette Edwards-Consolazio (CMU)
Sensor development for well corrosion monitoring	Paul Ohodnicki	Margaret Ziomonek-Moroz, Conjung Wang	
Cement integrity affected by acid mine water	Barbara Kutchko	James Gardiner, Alexandra Hakala	PA Department of Environmental Protection
Methane and radon migration in shallow aquifers	Daniel Soeder	AECOM	

Organization Chart: R&IC Onshore UCR
Water and Geochemistry Projects, 2 of 2

Proposed FY 2017 Projects

Task 2: Reservoir Processes, TTC: Dustin Crandall

Project	Principal Investigator
Organic, inorganic and isotopic analysis of fracture permeability changes	Alexandra Hakala
Reactive fracture flow tests	Alexandra Hakala
Characterization of key elements for mineral dissolution and precipitation	Christina Lopano
Ba precipitation control and Ba isotope development	Christina Lopano
Evaluation of microbial populations	Djuna Gulliver

Task 3: Wellbore Issues, TTC: Barbara Kutchko

Project	Principal Investigator
Evaluate cement samples from wellbore-acid mine water field scenarios	Barbara Kutchko
Synchrotron analysis of cement samples	Christina Lopano
Corrosion and stress wellbore sensor development	Paul Ohodnicki

Task 5: Water Issues, TTC: Alexandra Hakala

Project	Principal Investigator
Development of new isotope systems for fluid analysis	Alexandra Hakala
Electrochemistry-based techniques for trace metal determination in brines	Alexandra Hakala
Geochemical studies with drill cuttings	Christina Lopano
Modeling fate of drill cuttings leachate	Daniel Soeder
Geochemical testing and modeling of established isotope tracers in UOG basins	Alexandra Hakala
Water treatment for produced waters	Nicholas Siefert
Establish base to groundwater in U.S. shale basins	Kelly Rose
Produced water supply chain modeling	Robert Dilmore

Gantt Chart

	Project Dates for each Task/Subtask		FY16			
	Start	Finish	Q1	Q2	Q3	Q4
5. Water and Geochemistry	**10/01/2015**	**09/30/2020**				
5.1 Field Laboratories	10/01/2015	09/30/2020				
5.1.1 Fluid and solid isotope characterization at MSEEL	10/01/2015	09/30/2016	◄			►
5.1.2 Characterize chemistry of leachates from solid wastes when disposed under various conditions	10/01/2015	09/30/2016	◄			►
5.2 Fundamentals of Unconventional Oil and Gas Reservoirs	10/01/2015	09/30/2020				
5.2.1 Comparison of microbial ecology in Marcellus (dry gas) reservoir and the Bakken Petroleum System (oil, NGL, and gas)	10/01/2015	09/30/2016	◄			►
5.2.2 Biocide effectiveness through reactivity with shale minerals	10/01/2015	09/30/2016	◄			►
5.3 Wellbore Integrity	10/01/2015	09/30/2020				
5.3.2 Sensor development -- monitor potential casing corrosion downhole	10/01/2015	09/30/2016	◄			►
5.3.3 Evaluate effect of acidic, metal-laden mine waters on well casing and cement	10/01/2015	09/30/2016	◄			►
5.4 Protecting Water Resources	10/01/2015	09/30/2020				
5.4.1 Methane and radon migration in shallow aquifers as a site is developed	10/01/2015	09/30/2016	◄			►

Bibliography – FY 2016

- Journal Publications:
  - Dieterich, M.; Kutchko, B.; Goodman, A., 2016, Characterization of Marcellus Shale and Huntersville Chert before and after exposure to hydraulic fracturing fluid via feature relocation using field-emission scanning electron microscopy. Fuel, v. 182, p. 227-235.
- Additional Tech Transfer (details available upon request):
  - Conference Papers: 1
  - Inventions, Patent Applications, Licenses: 1
  - Presentations: 14
  - Publications (including *in preparation*): 18